

Global Water Research Coalition

N_2O and CH_4 emission from wastewater
collection and treatment systems
State of the Science Report

N₂O AND CH₄ EMISSION FROM WASTEWATER COLLECTION
AND TREATMENT SYSTEMS
STATE OF THE SCIENCE REPORT

REPORT

2011

29

ISBN 978.90.77622.23.0



COLOFON

Global Water Research Coalition
c/o International Water Association
Alliance House
12 Caxton Street
London SW1H 0QS
United Kingdom

GWRC 2011-29
ISBN 978.90.77622.23.0

Copyright by Global Water Research Coalition

DISCLAIMER

This study was jointly funded by GWRC members. GWRC and its members assume no responsibility for the content of the research study reported in this publication or for the opinion or statements of fact expressed in the report. The mention of trade names for commercial products does not represent or imply the approval or endorsement of GWRC and its members. This report is presented solely for informational purposes.

GLOBAL WATER RESEARCH COALITION

Global cooperation for the exchange and generation of water knowledge

In 2002 twelve leading research organisations have established an international water research alliance: the Global Water Research Coalition (GWRC). GWRC is a non-profit organization that serves as a collaborative mechanism for water research. The benefits that the GWRC offers its members are water research information and knowledge. The Coalition focuses on water supply and wastewater issues and renewable water resources: the urban water cycle.

The members of the GWRC are:

KWR – Watercycle Research Institute (Netherlands), PUB – Public Utilities Board (Singapore), STOWA – Foundation for Applied Water Research (Netherlands), SUEZ Environnement – CIRSEE (France), TZW – German Water Center (Germany), UK Water Industry Research (UK), Veolia Environnement VERI (France), Water Environment Research Foundation (US), Water Quality Research Australia (Australia), Water Research Commission (South Africa), Water Research Foundation (USA), and the Water Services Association of Australia.

The US Environmental Protection Agency has been a formal partner of the GWRC since 2003. The Global Water Research Coalition is affiliated with the International Water Association (IWA).

GWRC members represents the interests and needs of 500 million consumers and has access to research programs with a cumulative annual budget of more than 150 million. The research portfolio of the GWRC members spans the entire urban water cycle and covers all aspects of resource management.

PREFACE

The Global Water Research Coalition is an international organisation that is dedicated to the exchange and generation of knowledge to support sustainable development and management of the urban water cycle. The research agenda is developed by the member organisations of the GWRC and reflects their priorities and recognises global trends and drivers that affect the urban water cycle. The present research agenda includes Climate Change as one of the priorities areas. This research area comprises topics related to the possible impact of climate change on the urban water sector as well as the possible contribution to climate change by the urban water sector via the direct and indirect emission of greenhouse gasses (GHG).

The objective of this joint effort was to collect and develop knowledge needed to understand and manage the emission of N₂O (nitrous oxide) and CH₄ (methane) by wastewater collection and treatment systems. Starting with a kick-off meeting in Vienna in September 2008, the GWRC members involved in this activity have bundled their individual research programs on this topic, aligned methodologies used and exchanged and discussed the resulting information of the programs and developed additional actions where needed. The outcomes were reviewed and discussed at a final workshop in Montreal in September 2010.

These activities has resulted in two reports: a State of the Science report which presents an overview of the current knowledge and know-how regarding the emissions of N₂O and CH₄ by wastewater collection and treatment systems and a Technical Report which includes all the details, facts and figures of the underlying studies used to develop the State of the Science report.

GWRC expresses the wish that our joint effort and resulting reports will be useful to all who are active in the field of understanding and control of greenhouse gas emissions by wastewater collection and treatment systems.

Frans Schulting
Managing Director GWRC

ACKNOWLEDGEMENT

The Global Water Research Coalition wishes to express its appreciation to STOWA - Foundation for Applied Water Research (Netherlands) for acting as the GWRC's lead organisation for this joint effort and to recognise the high quality contributions by all organisations involved in this activity including Suez Environnement – CIRSEE (France), Water Environment Research Foundation (US), Water Research Commission (South Africa), and the Water Services Association of Australia. The support of the lead agent Stowa by Royal Haskoning is gratefully acknowledged as well.

The reports could not have been completed without the input and commitment of a number of individuals of the involved members of the GWRC and their associated organisations. These were:

AUTHORS

Jeff Foley
GHD
Australia



Zhigou Yuan
Jurg Keller
The University of Queensland
Australia



Elena Senante
CIRSEE-Suez
France



Kartik Chandran
Columbia University
USA



John Willis
Anup Shah
Brown and Caldwell
USA



Mark van Loosdrecht
Delft University of Technology
the Netherlands



Ellen van Voorthuizen
Royal Haskoning
the Netherlands



CONTRIBUTORS

Adam Lovell
WSAA
Australia



Lauren Fillmore
WERF
USA



Cora Uijterlinde
STOWA
the Netherlands



Gordon Wheale
UKWIR
UK



Pascal Dauthuille
CIRSEE-Suez
France



Jo Burgess
WRC
South Africa



SUMMARY

BACKGROUND

In a world where there is a growing awareness on the possible effects of human activities on climate change, there is a need to identify the emission of greenhouse gases (GHG) from wastewater treatment plants (WWTPs) (See Figure i). As a result of this growing awareness, some governments started to implement regulations that force water authorities to report their GHG emissions. With these developments, there exists a strong need for adequate insight into the emissions of N₂O (nitrous oxide) and CH₄ (methane), two important greenhouse gases. With this insight water authorities would be able to estimate and finally control their emissions. However, at this point few field data were available, with the result that the emission factors used by the Intergovernmental Panel on Climate Change (IPCC) were based on limited data. The lack of available data became the driver to start extensive research programs in Australia, France, the United States of America and the Netherlands with the objective to gain information needed to estimate, understand and control the emission of N₂O and CH₄ from wastewater collection and treatment systems.

FIGURE 1

GREENHOUSE GAS EMISSION FROM WASTEWATER TREATMENT PLANTS



CURRENT KNOWLEDGE

At the start of the research programs little was known about the processes which form N₂O, in contrast with the extensive knowledge on the formation of methane. In both cases, however, very little field data were available that gave insight on the level at which these two greenhouse gases were emitted from wastewater collection and treatment systems.

This lack of data resulted in the fact that the currently used IPCC emission factor for N₂O (3.2 g N₂O·person⁻¹·year⁻¹), which is used to estimate the N₂O emission from wastewater treatment plants, is based on only one field study in which the plant was not designed to remove nitrogen. Furthermore this lack of data has led the IPCC to conclude that: "wastewater in closed underground sewers is not believed to be a significant source of methane" (IPCC, 2006 a,b).

The data that has been published prior to the start of the research programs showed a very large variation in the level of N₂O emission. This is due to the fact that the formation of N₂O is a very complex process which can be performed by both nitrifying and denitrifying bacteria and is influenced by several process parameters. Denitrification in anoxic zones was in many cases indicated as the dominant source of N₂O emission from biological nitrogen removal processes.

JOINT EFFORTS

Since the topic of greenhouse gas emission from wastewater collection and treatment collection systems is of significance for the whole sector, the GWRC members¹ decided to join their individual research program results and support collaboration between their individual research partners. These joint efforts have led to an increased level of understanding on the processes forming N₂O emission from wastewater treatment facilities, the variety therein, and the contribution of methane emission from sewers and WWTPs. This increased level of understanding can already be used by the stakeholders of the GWRC members who are directly involved in the daily operation of wastewater collection and treatment systems.

Adjacent to the joint efforts of the GWRC members and individual research partners, the International Water Association (IWA) formed a Task group on the use of water quality and process models for minimising wastewater utility greenhouse gas footprints. The IWA Task Group is also collaborating with the GWRC researchers.

OBJECTIVES

The overall objectives of the different research programs were:

- Define the origin of N₂O emission.
- Understand the formation processes of N₂O.
- Identify the level of CH₄ emissions from wastewater collection and treatment systems.
- Evaluate the use of generic emission factors to estimate the emission of N₂O from individual plants.

BOUNDARIES

The main focus was to identify the level of emission, the variation therein and improve the knowledge of N₂O formation. Definition of mitigation strategies was outside the scope of most of the research as the knowledge on formation and origin was too limited at the start of the research programs.

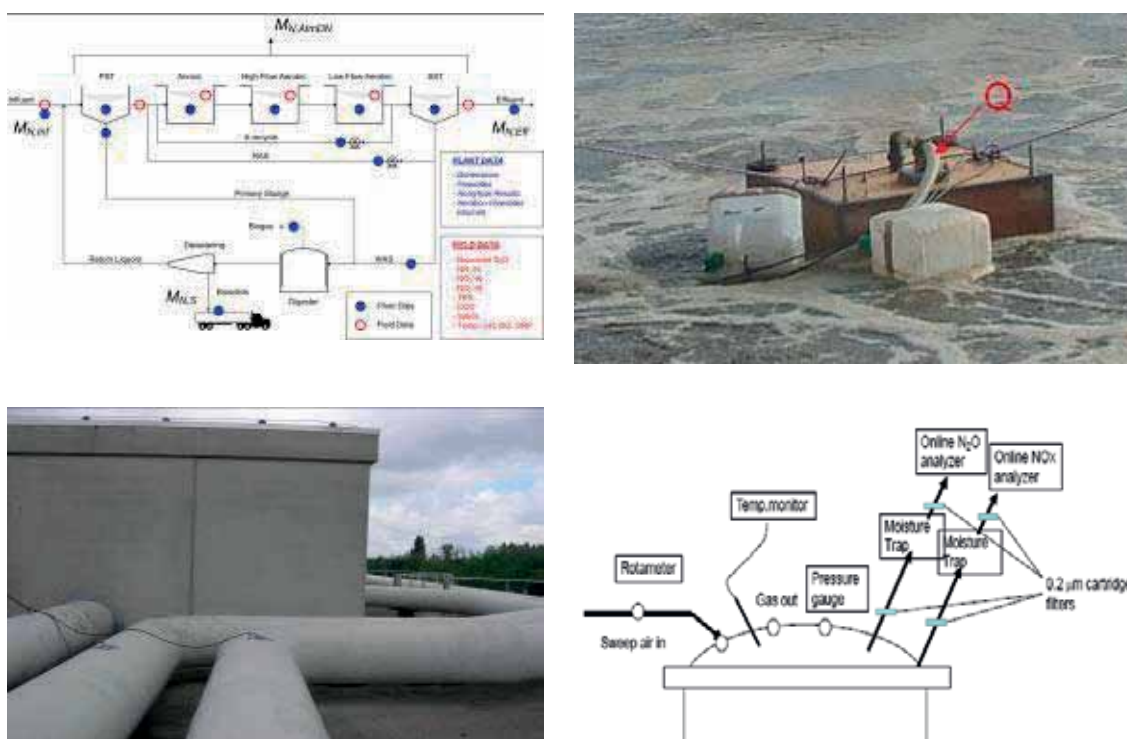
¹ GWRC members were (in brackets the partner that performed the research): WERF, USA (Columbia University, Brown and Caldwell); WSAA, Australia (The University of Queensland); STOWA, the Netherlands (Delft University of Technology; Royal Haskoning)

RESEARCH N₂O

METHODOLOGY

In all participating countries a wide range of WWTP types was selected with the expectation that differences between plant design and process conditions can help elucidate the factors influencing N₂O formation. The individual research partners used different methodologies (see Figure ii) to determine the emission of N₂O. The methodologies used in Australia, France, and the USA² were very suitable to gain insight in the formation processes of N₂O. The methodology used in the Netherlands, where the N₂O emission was measured in the total off-gas of covered WWTPs was very suitable to capture the variability of the emission. The use of different methodologies shows the complementary value of joint efforts to increase the level of knowledge on N₂O emission from WWTPs. For future work on this topic both methodologies will be required to finally estimate and control the emission of N₂O from WWTPs.

FIGURE II APPLIED METHODOLOGIES IN THE DIFFERENT RESEARCH PROGRAMS. STARTING IN THE LEFT CORNER ABOVE AND THEN CLOCKWISE: MASS BALANCE METHOD BASED ON LIQUID GRAB SAMPLES (AUSTRALIA); SAMPLING BOX FOR AERATED AREAS (FRANCE); TOTAL OFF-GAS MEASUREMENTS (THE NETHERLANDS); U.S. EPA, SURFACE EMISSION ISOLATION FLUX CHAMBER (SEIFC); (USA).



RESULTS

The emission of N₂O has been determined with different measurement protocols. For this reason it is not possible to average the emission numbers that have been derived. The results obtained in this research were suitable to increase the knowledge on N₂O formation and the variation therein, but the numbers can not be used to determine the emission from an individual plant as will be explained hereafter.

In line with earlier data, the field data in this study showed a large variety among the WWTP's

- 2 The protocol developed in the United States has been accepted by the USEPA, and is one of the most significant outputs of the research program.

sampled in the participating countries. The lowest emission that was measured was lower than 0.0001 kg N₂O-N/kg TKN_{influent}, while the highest reported emission was as high as 0.112 kg N₂O-N/kg TKN_{influent}. This led to the following conclusions:

- The N₂O emission is highly variable among different WWTPs and at the same WWTP during different seasons or throughout the day.
- The use of a generic emission factor to estimate the emission from an individual WWTP is inadequate
- The emission from an individual WWTP can only be determined based on online measurements over the operational range of the WWTP (i.e. lowest temperature, highest load etc).

On the origin of the emission results showed that:

- The emission of N₂O mainly originates from nitrification, in contrast with earlier information.

At the start of the different research studies, very little was known about the process parameters that influenced the formation of N₂O, and most of the knowledge was based on laboratory studies. The joint efforts of the GWRC members and their research partners led to an increased level of understanding of the formation of N₂O and the process parameters influencing formation. It was concluded that:

- Nitrite accumulation leads to the formation of N₂O in aerobic zones as a result of low oxygen levels, sudden changes in ammonium load, and higher temperatures.
- High ammonium concentrations can lead to the emission of N₂O if nitrification occurs.

The above conclusions could already be translated to practice, in a way that if high concentrations of nitrite, ammonium or dissolved oxygen can be avoided the risk of N₂O emission can be reduced. It was concluded that:

Systems that are not designed to remove nitrogen will have a high risk of N₂O emission if unintentional nitrification occurs.

With the present insight, it is possible to estimate the risk for N₂O emissions from a specific WWTP. This estimation can be based on the risk matrix presented in the following Table:

Parameter	Risk on N ₂ O		
	High risk	Medium risk	Low risk
Effluent total organic nitrogen (mg/l)	> 10	5 - 10	< 5
Range in N-concentration in plant	H	M	L
Load variations (daily)	H	M	L
Maximum NO ₂ concentration (mg N/l) anywhere in plant	> 0.5*	0.2 – 0.5	0.2

* Risk does not increase at higher NO₂ concentrations

Based on the above matrix and the other conclusions the major conclusion of the research performed on N₂O emission from WWTPs is:

A good effluent quality (TN < 5 mgN/l) goes hand in hand with a low risk of N₂O emission

REMAINING KNOWLEDGE GAPS AND FUTURE RESEARCH

Based on the outcomes of the research, valuable knowledge was gained to estimate and control the emission of N₂O from wastewater collection and treatment systems. The remaining knowledge gaps, their objectives and the type of research required are summarised as follows:

Knowledge gap	Objective	Future research
Insight in the variability of N ₂ O emission throughout the year at a WWTP to be able to define guidelines to design a sampling program at uncovered plants.	To obtain a good emission estimate of individual plants with minimal uncertainty.	Long term measurements in the total off-gas of WWTPs (covered ones are the most suitable to do so).
The relative contribution of autotrophic and heterotrophic processes to N ₂ O generation.	To develop mitigation strategies.	High resolution monitoring of liquid phase N ₂ O specific zones of WWTP.
Mitigation strategies.	To define measures to control emission via process design and control.	Measurements at different zones of one specific WWTP to study effect of different measures.
Emission from unknown sources like biofilm based processes and receiving aquatic environment.	To define level of N ₂ O emissions from these sources and to complete the picture of the whole urban watercycle.	Measurements at several locations that capture the variability that is expected.

RESEARCH CH₄

METHODOLOGY

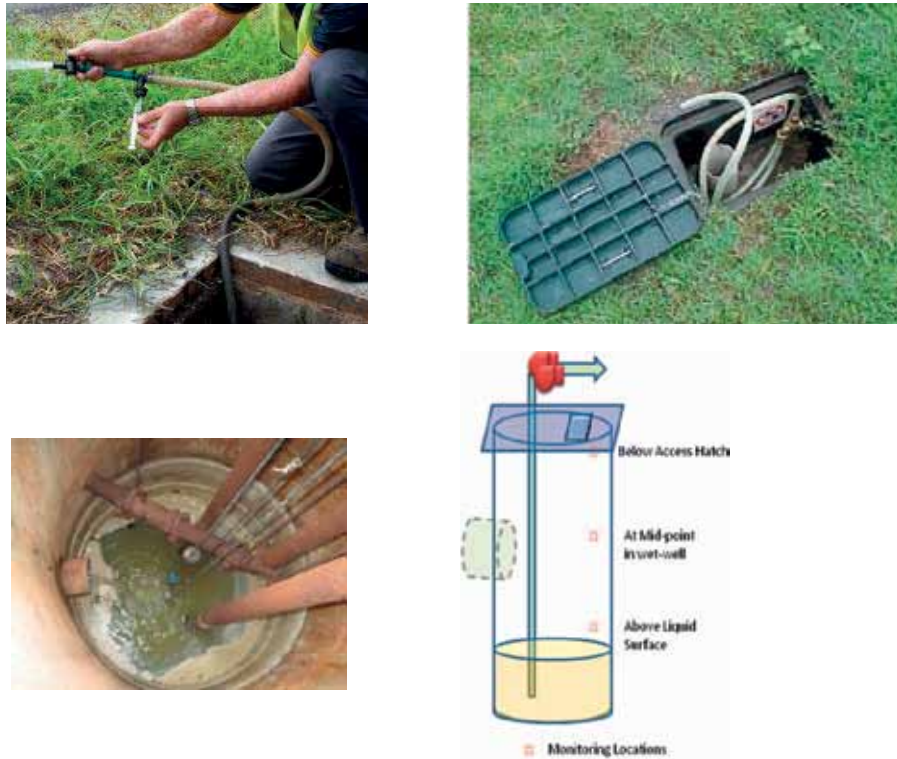
The emission of methane was determined both from wastewater collection and treatment systems. The emission from wastewater collection systems was performed in Australia and the United States of America (see Figure iii). In Australia measurements were made in the liquid and gas phase in or around raising mains. The gas phase of unventilated lift stations was analysed in a study from the United States of America. A major obstacle in finally determining the emission of CH₄ (kg/d) from sewers is the determination of the gas flow (m³/d). Developing a strategy for this obtaining flow measurement is one of the major research topics in this area. Mitigation strategies to control the emission of CH₄ from sewers were tested on laboratory and field level in Australia.

The emission of CH₄ from wastewater treatment systems was investigated in France and the Netherlands. In France, the emission of CH₄ was monitored via a gas hood that was placed at the surface of different zones in a WWTP.

The emission of CH₄ in the Netherlands was determined based on grab samples taken from the different process units. These samples were taken in the same period as the emission of N₂O was monitored. In this way the carbon footprint of a WWTP could be determined as the data of electricity and natural gas use were readily available.

FIGURE III

ABOVE: SAMPLING SYSTEM RISING MAINS (AUSTRALIA); UNDER: SAMPLING SYSTEM UNVENTILATED LIFT STATIONS (USA)



RESULTS

At the start of the research, very little was known about the level of CH₄ emission from sewers and WWTP; the emission from sewers was even neglected. The results showed that the methane concentration in the liquid and gas phase from wastewater collection and treatment can be substantial. Concentrations up to more than 30 mg/l in the liquid phase were reported and emissions from lift stations were found to be as high as ~700 kg CH₄/year, but also emissions close to zero were found. This led to the following conclusion:

- Formation and emission from wastewater collection systems can be substantial and should not be neglected.

Measurements to define the emission of CH₄ (i.e. kg/d) from sewerage systems were found to be very difficult and complicated. Development of a good strategy measurement is seen as an important research topic.

Furthermore, a start was made to find strategies that could control the emission of CH₄ from sewers. Based on these preliminary experiments it was concluded that:

- Odour mitigation strategies in sewers likely also supports reduced CH₄ formation.

The level of CH₄ emission from WWTPs varied greatly from almost zero emission (< 0.0004 kg CH₄-COD/kg COD_{influent}) to emissions as high as 0.048 kg CH₄-COD/kg COD_{influent}). In general it was concluded that:

- Emission of CH₄ from WWTPs mainly originates from CH₄ formed in sewers and from sludge handling processes.

REMAINING KNOWLEDGE GAPS AND FUTURE RESEARCH

Based on the outcomes of the research valuable knowledge was gained to estimate and control the emission CH₄ from wastewater collection and treatment systems. The knowledge gaps, their objectives and the type of research required are summarised as follows:

Knowledge gap	Objective	Future research
Strategy to determine amount of gas emitted to the air from wastewater collection systems.	To define the emission (kg/d) of CH ₄ from wastewater collection systems	Develop a strategy based on field data.
Field data from different type of wastewater collection systems around the world.	To make a good estimate of the contribution of wastewater collection systems. To deliver data for the development, calibration and validation of CH ₄ emission models.	Field measurements both liquid and gas phase from rising mains and gravity sewers around the world.
Cost effective mitigation strategies	To control the emission of CH ₄ from wastewater collection systems.	Experiments in practice to study the effects and costs of different mitigation strategies.
Emission from sludge treatment lagoons.	To define level of CH ₄ emissions from this source.	Measurements at several locations that capture the variability that is expected.

TOTAL CARBON FOOTPRINT

As a first indication on the possible contribution of N₂O and CH₄ emission to the total carbon footprint of a WWTP, the result in the Netherlands could be used as an example.

In the case studies in the Netherlands, the specific emissions of N₂O and CH₄ were determined at the same time. Together with the data on the related consumption of electricity and natural gas, it was possible to calculate a carbon footprint of three WWTPs. To determine the carbon footprint, all sources were converted to CO₂ equivalents³. The results in the Netherlands indicated that the emission of CH₄ and N₂O can significantly contribute to the total carbon footprint of a WWTP. This contribution can vary from 2% to almost 90% of the carbon footprint under extreme conditions for N₂O and 5 – 40% for CH₄. One should be aware that these numbers are specific for the Netherlands. In any other country, these numbers can differ greatly as there exist a great variation in the way wastewater and sludge is handled as well as the specific composition of the energy mix used. Furthermore these numbers can significantly differ depending on how the boundaries are set around the analysis. In case of the analysis performed for the three Dutch WWTPs the contribution of e.g. chemical use, and sludge incineration were not accounted for.

FUTURE ACTIVITIES

In the future the following activities will be developed by GWRC members and their researchers to further estimate and control the emission of GHG from wastewater collection and treatment systems:

- Long term measurements of both N₂O formation and process variables from one WWTP, to gain insight in N₂O formation processes and the variability throughout the year.
- Mitigation strategies to gain insight in the possibilities to control the emission via process design and control.
- Development of a predictive model on N₂O production and emission.

³ It should be noted that the conversion numbers are country specific and do depend on the used energy mix (i.e. brown coal versus wind or solar energy), which is of influence on the total carbon footprint of a WWTP.

DE STOWA IN BRIEF

The Foundation for Applied Water Research (in short, STOWA) is a research platform for Dutch water controllers. STOWA participants are all ground and surface water managers in rural and urban areas, managers of domestic wastewater treatment installations and dam inspectors.

The water controllers avail themselves of STOWA's facilities for the realisation of all kinds of applied technological, scientific, administrative legal and social scientific research activities that may be of communal importance. Research programmes are developed based on requirement reports generated by the institute's participants. Research suggestions proposed by third parties such as knowledge institutes and consultants, are more than welcome. After having received such suggestions STOWA then consults its participants in order to verify the need for such proposed research.

STOWA does not conduct any research itself, instead it commissions specialised bodies to do the required research. All the studies are supervised by supervisory boards composed of staff from the various participating organisations and, where necessary, experts are brought in.

The money required for research, development, information and other services is raised by the various participating parties. At the moment, this amounts to an annual budget of some 6,5 million euro.

For telephone contact number is: +31 (0)33 - 460 32 00.

The postal address is: STOWA, P.O. Box 2180, 3800 CD Amersfoort.

E-mail: stowa@stowa.nl.

Website: www.stowa.nl.

N₂O AND CH₄ EMISSION FROM WASTEWATER COLLECTION AND TREATMENT SYSTEMS

CONTENT

	GLOBAL WATER RESEARCH COALITION	
	PREFACE	
	ACKNOWLEDGEMENT	
	SUMMARY	
	STOWA IN BRIEF	
1	INTRODUCTION	1
1.1	Background	1
1.2	Objectives	1
1.3	Boundaries report	1
1.4	Outline report	2
2	CURRENT STATE OF KNOWLEDGE	3
2.1	N ₂ O formation	3
2.2	CH ₄ emission	3
2.3	Emission factors	4
	2.3.1 Nitrous oxide (N ₂ O)	5
	2.3.2 Methane (CH ₄)	5
3	REGULATIONS AROUND GREENHOUS GAS EMISSIONS	6

4	METHODOLOGY	8
4.1	Field sampling sites N ₂ O	8
4.2	Sample collection and analysis N ₂ O	8
4.2.1	Sample collection	8
4.2.2	Concentration	9
4.2.3	Gas flow	9
4.2.4	Additional data	10
4.2.5	Quality control	10
4.2.6	Calculations	11
4.3	Field sampling sites CH ₄	12
4.3.1	Sewers	12
4.3.2	WWTPs	12
4.4	Sample collection and analysis CH ₄	12
4.4.1	Liquid phase sample collection from sewers and analysis (Australia)	12
4.4.2	Sample collection and analysis gas phase sewers (USA)	13
4.4.3	Sample collection and analysis at WWTP	14
4.5	Mitigation strategies sewers	15
4.5.1	pH elevation	15
4.5.2	Nitrite addition	15
4.5.3	Iron salt addition	17
4.6	Total carbon footprint WWTP	17
5	RESULTS	18
5.1	N ₂ O emission from WWTPs	18
5.1.1	Emission of N ₂ O	18
5.1.2	Origin of N ₂ O emission	20
5.1.3	Process parameters of influence	22
5.2	CH ₄ emission from sewers	23
5.2.1	Liquid phase	23
5.2.2	Gas phase	24
5.2.3	Mitigation strategies	26
5.3	CH ₄ emission from WWTPs	30
5.3.1	Emission of CH ₄	30
5.3.2	Origin of emission	30
5.4	Total carbon footprint	32
6	DISCUSSION	33
6.1	Methodology	33
6.1.1	N ₂ O emission	33
6.1.2	CH ₄ emission	34
6.2	N ₂ O emission	34
6.2.1	Emission	34
6.2.2	Origin	34
6.2.3	Process parameters influence	35
6.2.4	Implications of gained knowledge	35
6.2.5	Future research	36
6.3	CH ₄ emission	36
6.3.1	Sewers	36
6.3.2	Mitigation strategies	36
6.3.3	WWTPs	37
6.4	Total carbon footprint WWTP	37

7	CONCLUSIONS AND FUTURE RESEARCH	38
7.1	Conclusions	38
7.1.1	N ₂ O emission	38
7.1.2	CH ₄ emission	38
7.1.3	Total Carbon Footprint	38
7.2	Future research	39
8	ACKNOWLEDGEMENTS	40
8.1	Australia methane research	40
8.2	Australia nitrous oxide research	40
8.3	United States of America nitrous oxide research	42
8.4	United States of America methane research	42
8.5	Research performed in the Netherlands	42
9	REFERENCES	43
	BIJLAGE	
1	SAMPLE COLLECTION WITH GAS HOODS	45
2	ABBREVIATIONS AND GLOSSARY	49
3	DEKALB COUNTY'S COLLECTION SYSTEM	51
4	CHARACTERISTICS WWTPS INVESTIGATED IN N ₂ O RESEARCH	53
5	RESEARCH AREA METHANE RESEARCH AUSTRALIA	57

1

INTRODUCTION

1.1 BACKGROUND

In a world where there is a growing awareness of the possible effects of human activities on climate change, there is a need to identify the emission of greenhouse gases (GHG) from wastewater treatment plants (WWTPs)⁴. As a result of this growing awareness, governments started to implement regulations that require water authorities to report their GHG emissions. With these developments there exists a strong need for adequate insight into the emissions of N₂O and CH₄. With this insight water authorities would be able to estimate and finally reduce their emissions. At the time little information was available on the formation of GHG, and the emission factors used by the IPCC are based on limited data. The limits of available data became the driver to start extensive field studies in Australia, France, the United States of America and the Netherlands with the objective to fill the knowledge gaps needed to estimate and reduce the emission of N₂O and CH₄ from wastewater collection and treatment systems.

The research programs were performed by partners⁵ of the GWRC members WERF (United States of America), WSAA (Australia), CIRSEE-Suez (France) and STOWA (the Netherlands).

1.2 OBJECTIVES

The overall objectives of the different research programs⁶ were:

- Define the origin of N₂O emission.
- Understand the formation processes of N₂O.
- Identify the level of CH₄ emissions from wastewater collection and treatment systems.
- Evaluate the use of generic emission factors to estimate the emission of N₂O from individual plants.

1.3 BOUNDARIES REPORT

The research described in this report was the first extensive research on N₂O and CH₄ emission from wastewater collection and treatment systems. The main focus was to identify the level of emission, the variation therein and improve the knowledge on N₂O formation.

Definition of mitigation strategies was outside the scope of most of the research as the knowledge on formation and origin was too limited at the start of the research. For methane some mitigation strategies were investigated and are reported here.

- 4 The greenhouse gases associated with the activities at WWTPs are CO₂, CH₄ and N₂O. Of these gases, N₂O is the most important as it has a 300-fold stronger effect than CO₂. CH₄ is less strong than N₂O but still has a 25-fold stronger effect than CO₂. Nitrous oxide (N₂O) can be formed during the conversion of nitrogenous compounds in wastewater; methane may be emitted in the sewer system and during sludge handling. The emission of CO₂ from the biological treatment is part of short cycle (or biogenic) CO₂ and does not contribute to the carbon footprint. However, some carbon in wastewater may originate from fossil fuel.
- 5 Partners were: Columbia University, USA; Brown and Caldwell, USA; The University of Queensland, Australia; Delft University of Technology, the Netherlands, Royal Haskoning, the Netherlands.
- 6 In the technical report (GWRC, 2011) that accompanies this State of the Art Report the objectives of the individual partners are mentioned.

1.4 OUTLINE REPORT

The current state of knowledge prior to the start of the research is summarised briefly in chapter 2. A summary of the regulations that apply in countries participating in the GWRC report is presented in chapter 3. In chapter 4, the applied methodologies to determine the emission of CH₄ and N₂O are presented. The results of the different research are presented in chapter 5, after which the results are discussed in chapter 6. Finally the conclusions and recommendations for further research are presented in chapter 7. The details of all research programs are described in a technical report (GWRC, 2011) and the following reports of the individual GWRC members were used:

- WERF: Chandran, K., 2010, Greenhouse nitrogen emission from wastewater treatment operations, WERF report U4R07a.
- WSAA: Foley, J., Lant, P., 2009, Direct Methane and Nitrous oxide emissions from full-scale wastewater treatment systems, Occasional paper No.24, Water Service Association of Australia.
- STOWA: Voorthuizen van, E.M., van Leusden, M., Visser, A., Kruit, J., Kampschreur, M., Dongen van, U., Loosdrecht van, M., 2010, Emissies van broeikasgassen van rwzi (in Dutch, summary in English), STOWA report 2010-08.

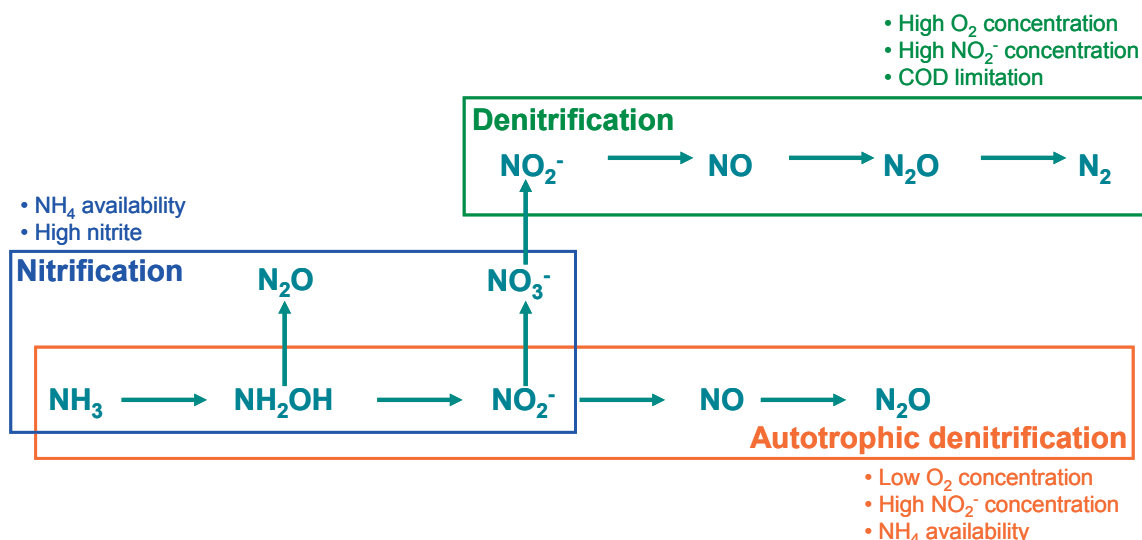
2

CURRENT STATE OF KNOWLEDGE

2.1 N₂O FORMATION

Nitrous oxide can be produced during the conversion of nitrogen in WWTPs. Based on an extensive literature review; three processes have been identified as the main processes by which N₂O can be formed. These processes are presented in Figure 1. In addition, N₂O can be formed by chemical denitrification or during co-oxidation of ammonia to NO and N₂O by methanotrophic micro-organisms (Kampschreur, 2010). The main process parameters positively influencing the formation of N₂O are presented also in Figure 1. Those process parameters were found in several research papers and are summarized and explained in several reviews (Kampschreur et al. 2009, Foley and Lant, 2008).

FIGURE 1 SCHEMATIC OVERVIEW OF THE POSSIBLE ROUTES OF N₂O EMISSION AND THE PROCESS PARAMETERS THAT WERE FOUND TO INFLUENCE THE FORMATION OF N₂O



Because of the different formation routes and the varying process parameters influencing those routes, a large variation in N₂O emission can be expected from full scale WWTPs. This is confirmed by the measurements that have been performed so far (Kampschreur et al., 2009). A variation between 0 – 15% of to the total nitrogen load of the WWTP was found to be emitted as N₂O (Kampschreur et al., 2009).

2.2 CH₄ EMISSION

In contrast to the formation of nitrous oxide, the formation of methane is very well known. However, little information is available on the amount of methane that is emitted from WWTPs and sewer systems. Prior to this research, only one study performed by Czepiel et al. (1993) measured the emission of methane from WWTPs. Data on emission of CH₄ from sewers

were first reported by Guisasola et al. (2008). However, the possibility of methane formation in sewers has been acknowledged for a long time.

Methane can only be formed under anaerobic conditions. In this respect emission of methane can be expected from:

- sewer systems
- influent works (formation in sewerage system, but emitted here);
- anaerobic / anoxic tanks as part of activated sludge systems;
- sludge digestion and handling;

Methane that is emitted from the influent works is formed in the sewer system. Little information is known about the amount of methane formed in sewers. This is in contrast with H₂S. In most cases the influent headworks is totally covered and emission of methane occurs after air treatment. Due to the anaerobic conditions in anaerobic and anoxic tanks methane might be formed. However, if there is a presence of aerobic zones methanogens will not survive.

At WWTPs that are equipped with an anaerobic sludge digester, methane can be emitted from different locations related to the digester. Methane can be emitted during the different processes of biogas combustion (leakages, incomplete combustion) or during storage of digested sludge. At WWTPs without sludge digesters methane formation is possible if the excess sludge is stored. The amount of methane emitted from these storage facilities will depend on the sludge retention time applied in the activated sludge system, the temperature and the level of dissolved methane, which in turn depends on the type of transport system prior to the WWTP.

Despite the presence of oxygen in the aeration tanks, methane can be emitted from these tanks. This is most likely methane that has been formed earlier in the process or in the sewer. The presence of methanogens in activated sludge has been proven by different authors (Lens et al., 1995 and Gray et al., 2002). In these studies it was proven that the contribution of the methane production by methanogens was very limited. Gray et al. (2002) reported 0.01 – 0.02% of the amount of carbon removed.

2.3 EMISSION FACTORS

The United Nations Framework Convention on Climate Change is the globally recognised basis for collective action on the reduction of anthropogenic greenhouse gas emissions (UNFCCC, 2007). One of the key obligations for signatory countries under the UNFCCC is the compilation of an annual national greenhouse gas (GHG) inventory, covering four general sectors (energy; industrial processes; agriculture, forestry and other land use; and waste). Emissions of methane and nitrous oxide from wastewater treatment and discharge are reported under the waste sector (IPCC, 2006b). However, GHG emissions are not usually measured directly, but estimated through the application of models that link emissions to data on observable activities (Foley and Lant, 2009).

2.3.1 NITROUS OXIDE (N₂O)

In the revised 1996 IPCC Guidelines the estimation methodology for N₂O emission from wastewater handling assumed minimal nitrogen removal during treatment, and hence all influent nitrogen is discharged to aquatic receiving environments where the nitrogen is converted. During this conversion, some of the discharged nitrogen will be emitted to the atmosphere as N₂O at a default factor of 0.01 kgN₂O-N/kgN discharged.

This value was revised in 2006 to 0.005 kgN₂O-N/kgN¹discharged (IPCC 2006a). In the same revision IPCC acknowledged that in many advanced WWTPs nitrogen removal occurs. The proposed default emission factor was 0.0032 kgN₂O·person⁻¹·yr¹(⁷), based on one full-scale study by Czepiel et al. (1995) on a basic secondary treatment plant without nitrogen removal.

The above mentioned IPCC guidelines are used by most countries to estimate the emission of N₂O from domestic WWTP for their national inventory reports (NIR). Andrews et al. (2009) examined ten country-specific NIRs, six countries used the IPCC default procedures, and four countries use their own factors.

2.3.2 METHANE (CH₄)

In the current IPCC guidelines only methane emission from wastewater treatment systems is considered, the contribution of methane from sewers is neglected as can be read in the IPCC guidelines: “wastewater in closed underground sewers is not believed to be a significant source of methane” (IPCC, 2006a).

For wastewater treatment systems a generalised approach is prescribed (IPCC, 2006a). The exact description can be found in the IPCC documents (IPCC, 2006a). In essence, the approach is a reconciliation of the estimated mass of methane produced in the treatment process, with the measured mass of methane captured in the associated biogas system. Any difference in these figures is assumed to be a loss of methane to the atmosphere.

The above mentioned procedure is used by most countries to estimate the emission of CH₄ from WWTPs for their national inventory reports (NIR). Andrews et al. (2009) examined 12 country-specific NIRs, eight countries used the IPCC default procedures.

⁷ Assuming a wastewater nitrogen loading of 16 g·person⁻¹·d⁻¹ for developed countries (i.e. high protein intake) (Tchobanoglous et al., 2003; IPCC, 2006a; DCC, 2008b), this equates to approximately 0.035% of the nitrogen load of the influent.

3

REGULATIONS AROUND GREENHOUSE GAS EMISSIONS

As stated in the introduction, governments around the world started to implement regulations on reporting and reducing the emission of greenhouse gases. A summary of the regulations in the countries, of which the research is described here, is presented below.

The following Act and Regulations define the legislative requirements for greenhouse gas reporting within **Australia** which also counts for the wastewater treatment sector:

- *The National Greenhouse and Energy Reporting Act 2007*, including amendments; and
- *The National Greenhouse and Energy Reporting Regulations 2008*, including amendments:

The Regulations provide detailed requirements for reporting under the Act, including definitions of operational control, facilities, the requirements for registration and the types of greenhouse gas emissions and energy consumption/production that have to be reported. More details can be found in the GWRC technical report (GWRC, 2011).

In the United States of America some regulations on the emission of GHG can affect the wastewater treatment sector in the future. Those regulations fall under the attainment New Source Review program of the federal Clean Air Act (CAA), the Prevention of Significant Deterioration (PSD) program, and the federal mandatory reporting rule, separate from the CAA, that applies in general to those stationary sources that emit more 25,000 MT CO₂e per year. The California Global Warming Solutions Act of 2006 affects the wastewater sector in California only. This Act establishes the first comprehensive GHG regulatory program in the United States, and commits California to achieving significant GHG emission reductions by 2020. With this act five regulatory measures are already directed at the water/wastewater sector including increasing water use efficiency, increasing water recycling, reduction in the magnitude and intensity of energy use in California's water systems, increased usage of urban runoff, increased renewable energy production from water systems and a public goods charge on water meters to pay for most of the above activities.

In **France** there are no specific regulations concerning GHG emissions for the water sector. Nevertheless, all industries/companies with more than 50 employees must perform a carbon footprint assessment (new law July 2010). In the case of wastewater treatment plants, the French EPA (ADEME) recommends taking into account direct emissions of CH₄ and N₂O.

Treatment of wastewater in the **Netherlands** is delegated to the Waterboard Authorities. These Waterboard Authorities are obliged to report the emission of greenhouse gases from wastewater treatment plants with a capacity higher than 136,360 p.e⁸ or from wastewater treatment plants that handle more than 50 tonne sludge per day (IPCC).

Since April 2010 the Dutch Waterboards signed a “Dutch Climate Agreement” with the government. Part of this agreement is that the waterboards committed themselves to reduce the emission of N₂O and CH₄ with 30% (equal to approximately 200 ktonne CO₂-equivalents from 1990 to 2020).

8 Based on 136 g total oxygen demand

4

METHODOLOGY

4.1 FIELD SAMPLING SITES N₂O

In total 26 WWTPs were monitored among the four countries participating in this research, namely, Australia, France, United States of America and the Netherlands. In all countries, a wide range of WWTP types was selected with the expectation that differences between plant design and processes conditions can help elucidate the factors influencing N₂O formation. Furthermore differences in climate conditions were taken into account for the selection of WWTPs in the USA and Australia. With respect to nitrogen and phosphorus removal, nine WWTPs removed phosphorus biologically, 21 were BNR systems and 5 of them were non BNR systems. The configurations that were present among the monitored WWTPs were: oxidation ditches (2), plug flow reactors (9), carrousel (5), SBR (1), MBR (1), and unknown (8). The characteristics of all WWTPs are summarised in Annex 4.

4.2 SAMPLE COLLECTION AND ANALYSIS N₂O

4.2.1 SAMPLE COLLECTION

Most WWTPs worldwide are not covered; therefore methods needed to be developed to determine the emission of N₂O. For uncovered WWTPs, the samples for the analyses of N₂O were collected via suspended gas hoods in the process basins. At WWTPs that were totally covered, samples could be collected from the total off-gas. More details of the sample collection in the different countries are summarised in Table 1.

TABLE 1 OVERVIEW OF SAMPLE COLLECTION FOR N₂O MEASUREMENTS

Country	Sample collection	Period	Time	Location in WWTP	Liquid / gas phase	Gas hood / Total off gas
Australia	Grab samples	Winter / Spring 2008; Ideally 4 rounds.	Per round: 2-4 hours per day for 2 days	Anaerobic, anoxic, aerobic zones	Liquid	-
France	Continuously	<i>Information not available</i>	<i>Information not available</i>	Anaerobic, anoxic, aerobic zones	Gas	Gas hood
USA	Continuously / Grab samples	Summer / early Fall & Winter / early Spring	1 day (1/min; gas phase) 4-5x day (liquid)	Anaerobic, anoxic, aerobic zones Geometric center	Liquid (grab) & Gas (grab and continuous)	Gas hood
Netherlands	Continuously	Fall / Spring / Winter	7 days	-	Gas	Total off gas

In France and the USA, the gas samples were collected via a suspended (floating) gas hood. The working principles of these gas hoods are presented in Appendix 1.

4.2.2 CONCENTRATION

The methods used to measure the concentration of N₂O in either the gas or liquid phase are summarised in Table 2.

TABLE 2 OVERVIEW USED METHODS TO MEASURE N₂O CONCENTRATION IN EITHER GAS OR LIQUID PHASE

Country	N ₂ O gas phase	N ₂ O liquid phase
Australia	-	Clark-type microsensor (N ₂ O 25 with 70µm outside tip diameter), Unisense A/S, Aarhus, Denmark
France	Servomex model 4210 gas analyser	Via liquid phase sampling*
USA	Infrared	Miniaturised Clark-type sensor with internal reference and guard cathode; Unisense A/S, Aarhus, Denmark
Netherlands	Infrared; Emerson Process management Rosemount Analytical	-

* Details of the analysis in Annex 2.

4.2.3 GAS FLOW

To determine the emission of N₂O, an accurate measurement of the gas flow is important. It is more complicated to measure the emission of N₂O from uncovered WWTPs than from WWTPs that are totally covered. The methods used at both covered and uncovered WWTPs are summarised below. More details on the gas hood as used in France and the United States of America can be found in Annex 2.

FRANCE

The resulting areal flow of gas measured is calculated from the concentration measured at the exit of the sampling system (N₂O or CH₄ in mg/m³ air) and from the air flow applied to the sampling system (m³/h). The flow is related to the sampling area (area of the flow chamber in the case of non-aerated surfaces or the area of the sampling box in case of aerated surfaces), and is expressed in mg.h⁻¹.m⁻². (For the working principle of the flow chamber and sampling box see Appendix 1).

UNITED STATES OF AMERICA

Sampling procedures-measurement of advective gas flow rate from aerated zones

Advective flow of gas through the flux-chamber (Q_{emission}) in aerated zones was measured using a modification of ASTM method D1946. Briefly, a tracer gas consisting of 100,000 ppmv (C_{helium-tracer}) He was introduced into the flux-chamber at a known flow rate, Q_{tracer} (equation 1). He concentrations in the off-gas from the flux-chamber (C_{helium-FC}) were measured using a field gas-chromatograph equipped with a thermal conductivity detector (GC-TCD). Q_{emission} was computed using equation 1.

$$Q_{\text{tracer}} * C_{\text{helium-tracer}} = (Q_{\text{tracer}} + Q_{\text{emission}}) * C_{\text{helium-FC}}$$

$$Q_{\text{emission}} = \frac{Q_{\text{tracer}} * (C_{\text{helium-tracer}} - C_{\text{helium-FC}})}{C_{\text{helium-FC}}} \quad (1)$$

Sampling procedures-measurement of advective gas flow rate from non aerated zones

The only modification to the protocol to measure the emission flow rate from *non-aerated zones* was the introduction of sweep gas (air) or carrier gas through the flux-chamber at a known flow rate (Q_{sweep}), in addition to the He tracer gas. The corresponding Q_{emission} was computed using equation 2. Addition of sweep gas is needed to promote mixing of the SEIFC (Surface emission isolation flux chamber) contents, owing to the low advective gas flow from the

anoxic-zone headspace. Sweep-air N₂O concentrations were always measured and typically below the detection limits of the N₂O analyzer.

$$Q_{\text{tracer}} * C_{\text{helium-tracer}} = (Q_{\text{tracer}} + Q_{\text{sweep}} + Q_{\text{emission}}) * C_{\text{helium-FC}} \quad (2)$$

$$Q_{\text{emission}} = \frac{Q_{\text{tracer}} * (C_{\text{helium-tracer}} - C_{\text{helium-FC}})}{C_{\text{helium-FC}}} - Q_{\text{sweep}}$$

During continuous N₂O measurements, Q_{emission} was determined several times a day.

THE NETHERLANDS

The flow of off gas through the pipes was measured using a pitot tube. The pitot tube was connected to a pressure probe (Testo 445, max. 10 hPa, accuracy +/- 0.03 hPa), which transferred the pressure difference to a gas velocity. In this way the gas velocity was measured at least three times during the measuring campaign. During each measurement the gas velocity was measured at 20 – 50 individual points throughout the whole pipe. Based on the internal diameter of the pipe the gas flow was calculated. The pitot tube was used during the measurement campaigns in Papendrecht and Kralingseveer. During the measuring campaign at Kortenoord, the gas velocity was measured with a hot wire anemometer (Testo 435-1, max. 20 m/s, accuracy +/- 0.03 m/s and +4% of measuring value). After the measurements, the error of the measurement was determined. If this error was larger than the variation in the gasflow, the emission was calculated with an average gasflow, if the error was smaller than the emission was calculated with the daily gasflow.

4.2.4 ADDITIONAL DATA

During all measuring campaigns, additional data which could be related to the emission of N₂O were collected to monitor the performance of the plant.

The additional data that were collected are:

- WWTP characteristics (process elements, volumes etc.);
- Influent, effluent composition and sludge concentration;
- On-line data from the available sensors at the WWTP.

Detailed information about the exact analyses and collection methods for the additional data can be found in the different research reports (Foley et al., 2009, Chandran 2010 and van Voorthuizen et al., 2010).

4.2.5 QUALITY CONTROL

The analysers used in the different research (Australia and the Netherlands) were calibrated prior to every measuring campaign. Details about the calibration methods can be found in the different research reports (Foley et al., 2009, Chandran 2010 and van Voorthuizen et al., 2010). The protocol that was developed for the measurements in the USA was validated in a special program in which the protocol was compared with other measuring methods. Details about this validation can be found in the different research reports (Foley et al., 2009, Chandran 2010 and van Voorthuizen et al., 2010).

4.2.6 CALCULATIONS

The emission of N₂O was in general calculated using the following formula:

$$\text{Emission} = \frac{[\text{N}_2\text{O}] \cdot Q_{\text{gas}} \cdot 24}{Q_{\text{influent}} \cdot [\text{TKN}]} \quad (3)$$

In which:

- [N₂O] is the concentration in the gas phase, either expressed as g N₂O or N₂O-N/m³
- Q_{gas} is the gas flow expressed as m³/h
- Q_{influent} is the influent flow to the WWTP expressed as m³/d
- [TKN] is the concentration NKj in the influent expressed as gN/m³

In Australia the concentration of N₂O in the gas phase was determined based on the liquid phase measurements and k_La values. These k_La values were determined at laboratory scale and were corrected for the circumstances at full scale plants. More details about this methodology can be found in the research report (Foley, J. et al., 2009)

In the United States the surface flux calculated from the flux chamber was translated into the flux of a given zone by multiplying over the specific zone area.

4.3 FIELD SAMPLING SITES CH₄

4.3.1 SEWERS

AUSTRALIA

Two measurement campaigns have been performed on the emission of methane from sewers. One measurement campaign was performed in Australia, where liquid phase measurements were performed in two rising mains. In this report the result of one of the rising mains will be presented. This rising main (CO16⁹) is situated at the Gold Coast, Queensland, Australia (see Figure 23 in Annex 5). Samples were taken at four sampling points (Pumping Station, Sample Points 1, 2 and 3) and sampling was repeated four times at an interval of one hour. In this way it was possible to capture wastewater samples with HRT in the sewer line for 0 – 8.7 hours.

UNITED STATES OF AMERICA

In the USA, gas phase measurements were performed in 64 lift stations on a force main system. The lift stations were predominantly fed by gravity sewers and in more limited cases by rising mains or a combination of the two.

The lift stations are situated in DeKalb County, Georgia, from which 60 are small with capacity ranging from 80 to 700 gallons per minute (gpm) (0.3 – 2.6 m³/minute) and 4 are large with firm capacities of over 2,000 gpm (~7.6 m³/min). Only one of the 64 lift stations is ventilated the other 63 are unventilated. An overview of DeKalb County and the locations of the 64 lift stations is presented in Appendix 3. The measurements were performed in a both cold (31 March – 4 April 2009) and warm (13 – 17 July 2009) periods.

4.3.2 WWTPS

The emission of methane from WWTPs was investigated in France and the Netherlands. For both countries counts that the WWTPs investigated were the same as for the N₂O measurements (see section 4.1)

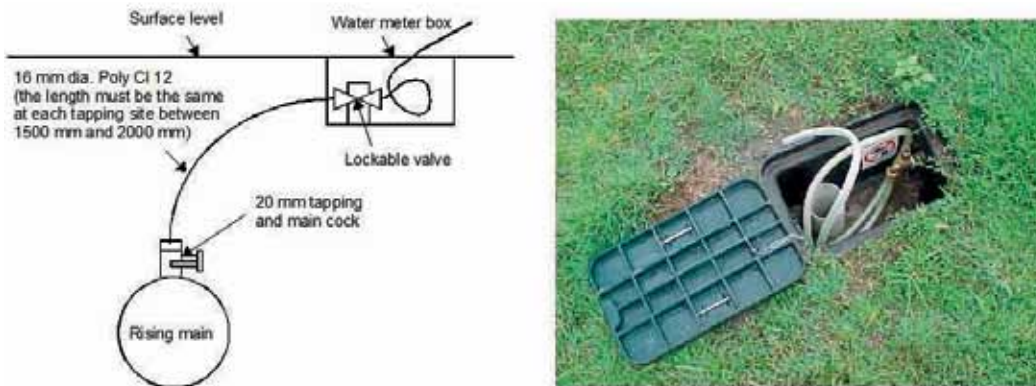
4.4 SAMPLE COLLECTION AND ANALYSIS CH₄

4.4.1 LIQUID PHASE SAMPLE COLLECTION FROM SEWERS AND ANALYSIS (AUSTRALIA)

Wastewater sampling from rising mains was done through a special sampling arrangement (Figure 2). It consists of a 16 mm diameter pipe connecting a sampling tap at the ground level to the tapping arrangement attached to the underground pipe.

Samples were collected using a hypodermic needle and 5 ml plastic syringe, attached directly to the pressurized rising main via a flexible hose. This procedure avoided any contact of the wastewater with atmosphere and possible oxygen interference.

⁹ The CO16 rising main receives domestic wastewater. It has an internal pipe diameter of 300 mm, giving an A/V ratio of 13.3 m⁻¹. The average daily wastewater flow was approximately 700 m³. The pumping station was operated intermittently with 30 -40 pumping events per day, each lasting for 4 – 6 min in duration. During each pumping event, the calculated flow velocity was approximately 0.90 – 1.01 m/s.

FIGURE 2 SAMPLING SYSTEM FOR RISING MAINS TO DETERMINE CONCENTRATION OF CH₄ IN LIQUID PHASE.

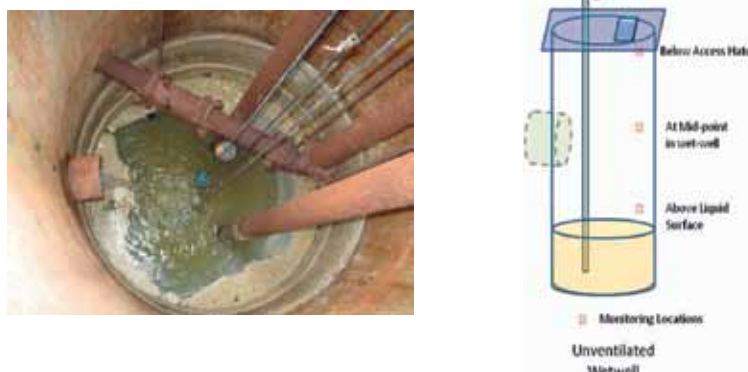
A sample collected was subsequently injected into freshly vacuumed BD Vacutainer[®] tubes through a 0.22 μm pore diameter unit (Millipore, Millex GP). The Vacutainer tube was mixed overnight in a shaker to allow equilibration of gas and liquid phases. Most of the methane (~97% at 25 °C) would be transferred to the gas phase in this process (Alberto et al., 2000). The methane concentration in the gas phase of the tube was measured using a Shimadzu GC-9A Gas Chromatograph equipped with a flame ionization detector (FID). The concentration of methane in the initial liquid phase was then calculated using mass balance and Henry's law (Guisasola et al., 2008). The Vacutainer tube was weighed before and after sampling to determine the sample volume collected. This volume, along with the known volume of the Vacutainer tube, enables to calculate dissolved methane contained in the original wastewater sample.

4.4.2 SAMPLE COLLECTION AND ANALYSIS GAS PHASE SEWERS (USA)

SAMPLE COLLECTION IN UNVENTILATED LIFT STATIONS

Figure 3 shows the inside of a typical unventilated lift station in the DeKalb collection system. CH₄ concentrations were measured at three locations in each wet well during each sampling event: immediately above the liquid surface, mid-way up the wet well headspace; and immediately below the access hatch. While all three concentrations were collected, the highest of the three was used in order to somewhat mitigate the lack of accounting for dispersion of lighter-than-air CH₄ in between pumping cycles or the air dilution that results when air is pulled into the well during a pumping cycle. A similar procedure for data collection was used at large unventilated lift stations with open fore bays including LCC PS-3 and Honey Creek.

FIGURE 3 SAMPLING METHOD USED AT UNVENTILATED LIFT STATIONS



SAMPLE COLLECTION IN VENTILATED LIFT STATIONS

There is only one ventilated lift station within DeKalb's collection system. At LCC-1 the wetwell is covered and foul air exhaust fans continuously withdraw air and send it to an odor control system. Openings for the influent screens and at the wetwell covers allow air to enter the wetwell as foul air is exhausted. Instantaneous measurements for CH₄ and other parameters were sampled directly from the discharge header of the exhaust fan upstream of the biofilter.

ANALYSIS

Portable instruments were used for taking instantaneous readings in the field. A hand-held flame ionization detector (FID, MicroFID manufactured by PhotoVac) with hydrogen as a fuel source was used to measure CH₄. A portable four-gas analyzer with photoionization detector (PID, RKI Eagle Gas Portable Monitor) was used to measure H₂S, CO₂, %lower explosive limit (LEL) and CO. Ambient air and raw sewage temperatures were also monitored to check for a correlation with the measured CH₄ concentration. A dissolved oxygen (DO) probe (YSI 550A DO) was used to measure ambient air temperature, raw sewage temperature, and dissolved oxygen concentration in the raw sewage.

4.4.3 SAMPLE COLLECTION AND ANALYSIS AT WWTP

FRANCE

The measurement of methane at the WWTPs in France was performed with the same set-up as for the N₂O measurements as described in 4.2.1.

THE NETHERLANDS

Grab samples for the analysis of the methane concentration were taken at the major process units of the WWTP. The location of and the amount of grab samples taken at each WWTP are summarized in Table 3. The grab samples were analyzed for CH₄ at the laboratory using gas chromatography (Varian CP-3800 Gas Chromatograph). The gas flow was determined in the same way as for the emission of N₂O (see section 4.2.3).

TABLE 3 SUMMARY LOCATIONS METHANE MEASUREMENTS AND NUMBER OF SAMPLES TAKEN

WWTP	Sample location	Number of samples	
Papendrecht	After inlet work and coarse screen	3	
	Selector	2	
	Anaerobic tank	2	
	Sludge loading	1	
	Carrouseles	1	
Kortenoord	After inlet work and coarse screen and grid removal	5	
	Selector	5	
	Aeration tank (3 channels N ₂ O measurements)	3	
	Sludge thickeners	3	
	Sludge storage	3	
Kralingseveer	Sludge dewatering site	4	
		October	February
	After inlet work and coarse screen	2	3
	Primary settling	2	3
	Selector	2	3
	Sludge thickeners	2	3
	Sludge storage	2	3
	Aeration tank	2	2
	Carrousel 1 and 2	2	3

The emission of CH₄ is based on the following measurements:

- CH₄ concentration in grab samples;
- Gas flow;
- Influent flow;
- COD concentration influent (after primary settling, including internal flow).

The CH₄ emission was calculated based on the average concentration in the grab samples. In almost all cases¹⁰ the average concentration was multiplied by the average gas flow as the error in the measurements was larger than the variations in the gas flow.

4.5 MITIGATION STRATEGIES SEWERS

Chemical dosage or pH elevation to sewage is commonly used for the control of sulphide formation in sewers, or its transfer from wastewater to sewer air.

The effect of pH elevation and the dosage of nitrite and iron salts on methane formation by sewer biofilms has been studied recently at the University of Queensland, Australia. The used methodologies are presented here.

4.5.1 PH ELEVATION

pH elevation through the addition of magnesium hydroxide (Mg(OH)₂) is commonly used as a means for reducing H₂S emission from wastewater to sewer air. When pH is elevated from a neutral level, which is typically in sewage, 8.5 – 9, the molecular hydrogen sulphide (H₂S) fraction of total dissolved sulphide is reduced, and as a result, it's transfer from the liquid to the gas phase is reduced.

Experiments were carried out on laboratory scale sewer systems consisting of both an experimental and a control reactor. Each reactor, with a volume of 1 l, was fed with domestic wastewater every six hours. During each pumping event, 1 l of wastewater was pumped into each reactor, resulting in a hydraulic retention time (HRT) of 6 hours. The 12-month experimental study was divided into four phases with conditions summarized in Table 4.

TABLE 4 EXPERIMENTAL CONDITIONS APPLIED DURING THE ENTIRE COURSE OF THE PH STUDY (GUTIERREZ ET AL., 2009)

Operational phases	Length (days)	Control Reactor	Experimental Reactor
1	0 - 40	No pH control 7.6±0.1	No pH control 7.6±0.1
2	51 - 110	No pH control 7.6±0.1	pH adjusted to 8.6±0.1 with 88 ml 0.05M NaOH in each pumping event
3	111 - 170	No pH control 7.6±0.1	pH adjusted to 9.0±0.1 with 120 ml 0.05M NaOH in each pumping event
4	171 - 332	No pH control 7.6±0.1	No pH control 7.6±0.1

4.5.2 NITRITE ADDITION

Experiments were carried out both on laboratory systems and in practice. The methodology of both experiments is described underneath.

LABORATORY EXPERIMENTS

The experimental set up for the experiments at laboratory scale (Jiang et al., 2010) is shown in Figure 4. This set up consisted of four air-tight reactors, namely R1 to R4, each with a volume of 0.75 l. The reactors were fed with sewage through a peristaltic pump every 6 hours, a typical

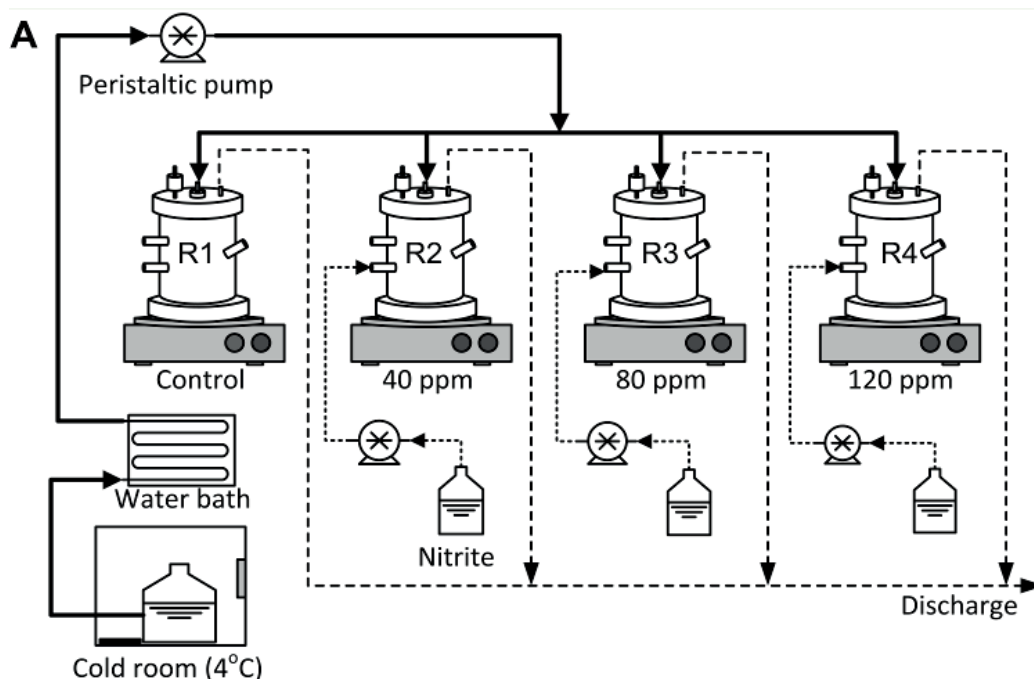
10 Exceptions were selector Papendrecht and sludge storage in Kralingseveer (February), here the daily gas flow was used.

sewage hydraulic retention time in sewers (Hvitved-Jacobsen, 2002). Every feed pumping event lasted for 2 minutes, delivering one reactor volume (0.75 l) of sewage into each reactor.

The experiments were conducted in three consecutive phases, namely the stabilization, dosing, and recovery phases. Reactors were operated without nitrite dosing to achieve similar sulphide and methane production activities during the stabilisation phase. During the dosing phase, R2-R4 received nitrite, while R1 was used as the control reactor (no nitrite dosage). Reactors R2-R4 were injected with nitrite to reach concentrations of 40, 80, and 120 mg-N/l of wastewater, respectively. After the 24-day dosing phase, nitrite dosing to R2 - R4 was stopped and the reactors were allowed to recover for two and half months (Recovery phase).

FIGURE 4

SCHEMATIC OF THE LABORATORY-SCALE RISING MAIN SEWER REACTORS. R1 DID NOT RECEIVE NITRITE, AND SERVED AS A CONTROL. R2, R3 AND R4 RECEIVED NITRITE AT 40, 80 AND 120 MGN PER L OF WASTEWATER FED, FOR A PERIOD OF 24 DAYS, WHICH WAS FOLLOWED BY A 2.5 MONTH RECOVERY PERIOD



FIELD TRIAL

A field trial was conducted to test intermittent nitrite dosing as a means for sulphide and methane control in a real sewer line, UC09, located in Gold Coast, Australia. This sewer line has a length of 1080 m and a diameter of 150 mm. It receives primarily domestic wastewater with an average daily flow of approximately 200 m³. The hydraulic retention time of sewage in the rising main varied between 1.7 and 5.7 hours during the period of the study.

Nitrite solution was dosed into the UC09 wet well manually during daytime only (8:00 AM to 7:00 PM) over three consecutive days. Before each pumping event, nitrite was added to the wet well, resulting in a concentration in sewage of 100 mg-N/l, a level determined based on the lab-scale reactor test results (Jiang et al., 2010). The dosage was stopped after three days. Therefore, the actual dosage time was 33 hours over a three day period.

Prior to nitrite dosing, three measurement campaigns were conducted to monitor methane production in the rising main over a period of seven days. Each campaign involved sampling wastewater hourly at both the pumping station wet well and 828 m downstream of the pumping station, for a period of 3 – 6 hours.

The samples were analyzed for dissolved methane concentrations using the method described in section 4.4.1. Similar measurement campaigns were also conducted 1, 4, 5, 10 and 13 weeks after nitrite dosing.

4.5.3 IRON SALT ADDITION

Two lab-scale rising main sewer systems fed with real sewage were operated for 8 months. One received Fe³⁺ dosage at 15 mg per l of wastewater (experimental system) and the other was used as a control (no Fe³⁺ dosage). (Zhang et al., 2009)

4.6 TOTAL CARBON FOOTPRINT WWTP

In the research performed in the Netherlands the emission of N₂O and CH₄ was measured at the same three WWTPs. Based on these measurements it was possible to determine the contribution of N₂O and CH₄ to the total carbon footprint of a WWTP including the use of electricity and natural gas. To determine the total carbon footprint of a WWTP all sources were converted to CO₂ equivalents. The conversions factors that have been used in this case are summarised in Table 5.

TABLE 5 CONVERSION FACTORS FOR CLIMATE FOOTPRINT CALCULATIONS USED IN THE NETHERLANDS

	Conversion factor	Unit
Electricity	0.67	kg CO ₂ /kWh
Natural gas	1.8	kg CO ₂ /Nm ³
N ₂ O	298 ¹⁾	kg CO ₂ /kg N ₂ O
CH ₄	25 ¹⁾	kg CO ₂ / kg CH ₄

1) GWP AR4: Adjusted GWP in IPCC Fourth assessment report, 2007 (IPCC,2007)

The conversion factors mentioned for electricity and natural gas in Table 5 are specific for the situation in the Netherlands. In any other country, other factors apply depending on the energy mix used.

The total carbon footprint analysis did not account for the CO₂ required to produce chemicals nor did it account for the emission of greenhouses gases emitted at the sites where the sludge was further handled (i.e. incinerated or composted).

5

RESULTS

5.1 N₂O EMISSION FROM WWTPS

5.1.1 EMISSION OF N₂O

The emission of N₂O as measured at all the different WWTPs in Australia, France, USA and the Netherlands is summarised in Table 6.

TABLE 6 OVERVIEW N₂O EMISSION AT THE SURVEYED WWTPS AROUND THE WORLD (VALUES PRESENTED IN BOLD ARE REPORTED OUTLIERS; FOR MORE DETAILS SEE TECHNICAL REPORT (GWRC,2011))

Country	WWTP	Sample round	Emission (kg N ₂ O/kg TKN _{influent})	Emission (kg N ₂ O-N/kg TKN _{influent})
Australia	1 – Ox. Ditch	1	0.005	0.003
		2	0.003	0.002
		3	0.006	0.004
		4	0.003	0.002
	2 – Johannesburg	1	0.016	0.010
		2	0.027	0.017
		3	0.011	0.007
	3 – SBR	1	0.009	0.006
		2	0.011	0.007
		3	0.050	0.032
	4 – MLE (1)	1	0.019	0.012
	5 – MLE (2)	1	0.014	0.009
		2	0.047	0.030
		3	0.006	0.004
		4	0.055	0.035
	6 – MLE (3)	1	0.176	0.112
		2	0.008	0.005
		3	0.005	0.003
	7 – A ² O	1	0.011	0.007
		3	0.006	0.004
France	WWTP 1		<0.0002	<0.0001
	WWTP 2		<0.0002	<0.0001
	WWTP 3		0.003	0.0017
	WWTP 4		0.002	0.0011
USA	Separate-stage BNR	1 (15°C)	0.0005	0.0003
		2 (23°C)	0.0002	0.0001
	Four-stage Bardenpho	1 (14°C)	0.0025	0.0016
		2 (23°C)	0.0094	0.006
	Step-feed BNR 1	1 (19°C)	0.025	0.016
		2 (25°C)	0.0097	0.0062
	Step-feed non-BNR	1 (17°C)	0.0028	0.0018
		2 (26°C)	0.028	0.018
	Separate centrate ¹⁾	1 (30°C)	0.0038	0.0024
		2 (34°C)	0.0085	0.0054
	Plug-flow 1	1 (11°C)	0.0063	0.004
		2 (23°C)	0.0064	0.0041
	Plug-flow 2	1 (11°C)	0.0097	0.0062
		2 (22°C)	0.0014	0.0009
	MLE 1	1 (26°C)	0.0011	0.0007
	MLE 2	1 (26°C)	0.0009	0.0006
	Step-feed BNR 2	1 (29°C)	0.024	0.015
	Oxidation ditch	1 (19°C)	0.0005	0.0003
Netherlands	Step-feed BNR 3	1 (24°C)	0.0008	0.0005
	Papendrecht	1 (19°C)	0.00063	0.00040
	Kortenoord	1 (19°C)	0.00075	0.00048
	Kralingseveer	1 (18°C)	0.0066	0.0042
		2 (10°C)	0.096	0.061

1) Not a typical WWTP

Based on the emission data presented in Table 6 the following observations can be made:

- The emission of N₂O varies greatly among WWTPs measured, the lowest emission was smaller than 0.0001 kg N₂O-N / kg TKN_{influent} the highest emission was as high as 0.112 kg N₂O-N / kg TKN_{influent}.
- The emission at the different WWTPs per country differs greatly depending on configuration and operations.
- The emission varies in between seasons as shown by the results from the USA and the Netherlands

Besides the observed variations in N₂O emission mentioned above, a strong variation was observed during a day at one WWTP. An example of this from the WWTP Kralingseveer, the Netherlands is presented in Figure 5. It can be observed that the emission of N₂O varied with the influent flow. This suggests that the emission of N₂O is related to the variation in sludge load. A similar relation was found in the USA study, where the diurnal variability observed could be linked to diurnal variations in influent N-loading (Ahn et al., 2009). An example of this is presented in Figure 6.

FIGURE 5 N₂O EMISSION AND INFLUENT FLOW ON 18-10-2008 AT WWTP KRALINGSEVEER

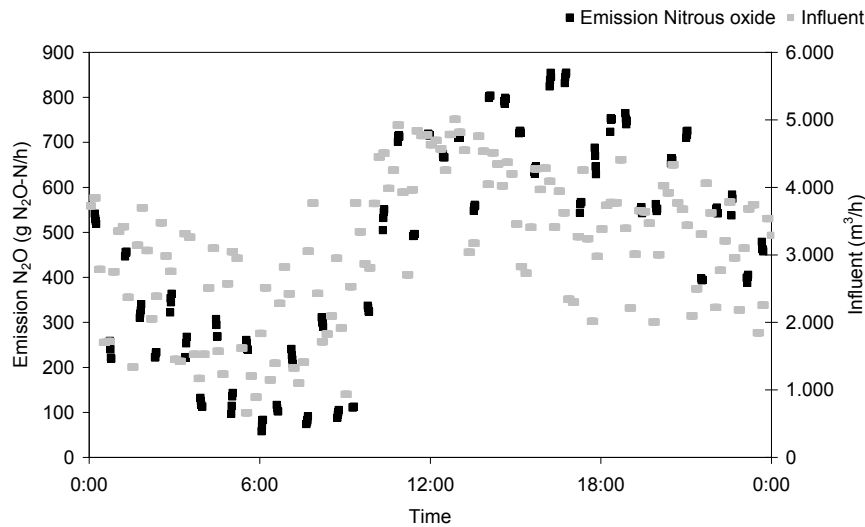
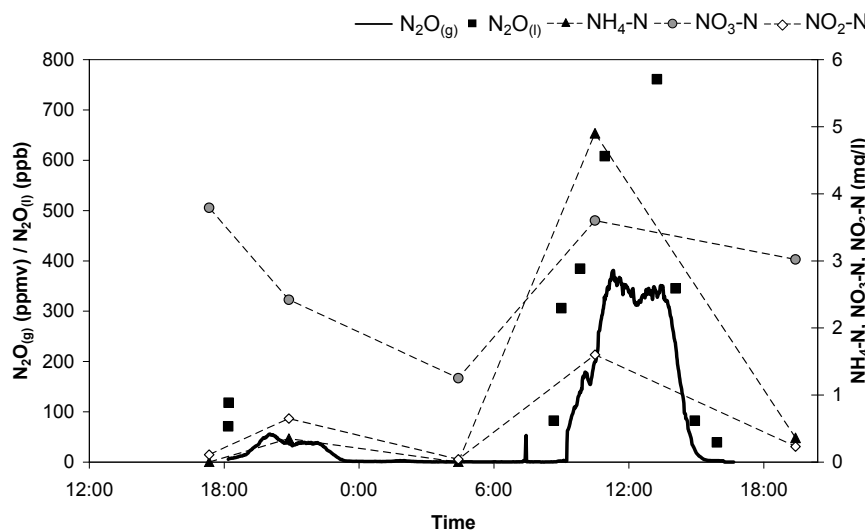


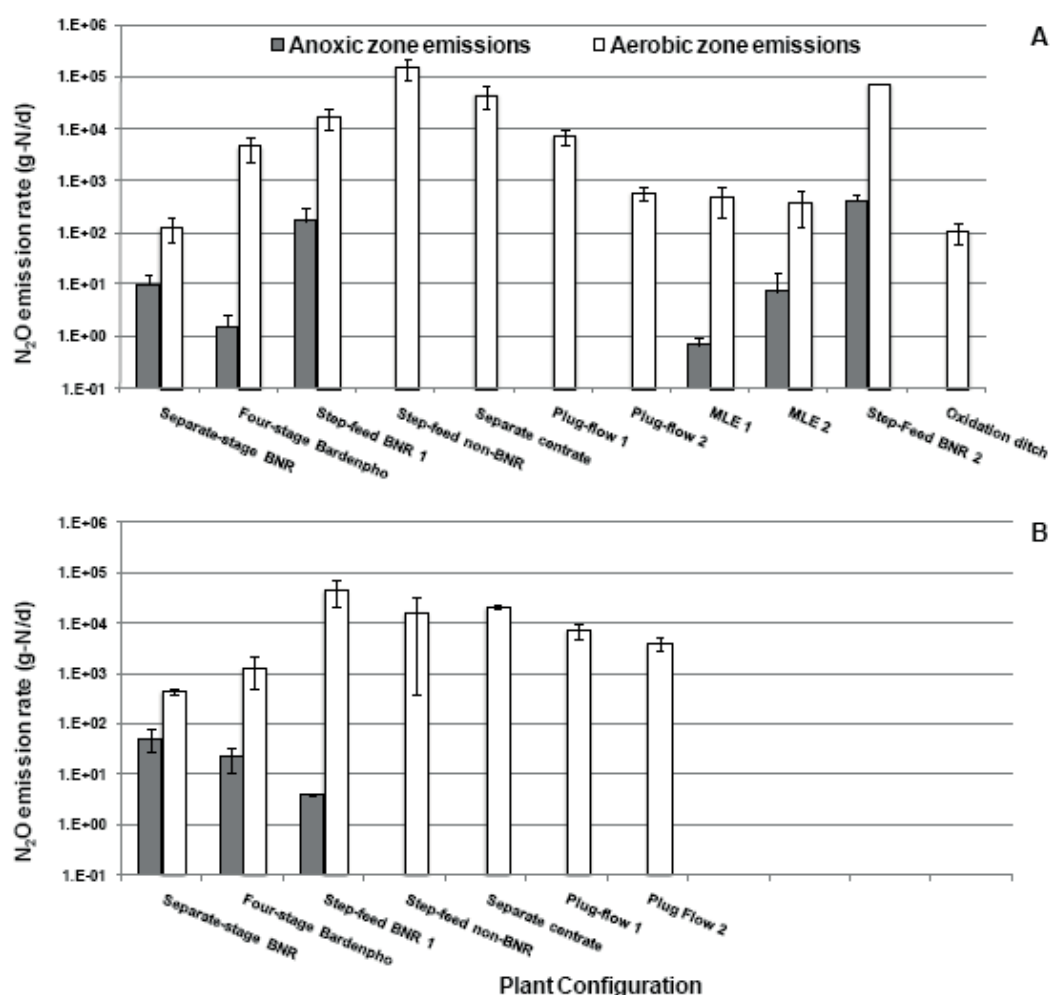
FIGURE 6 DIURNAL VARIABILITY IN GASEOUS N₂O CONCENTRATIONS MEASURED FROM AN AEROBIC ZONE OF THE FULL-SCALE STEP-FEED BNR PROCESS



5.1.2 ORIGIN OF N₂O EMISSION

N₂O can be formed and emitted from anoxic and aerobic zones, i.e. N₂O can be formed during both denitrification and nitrification. Based on the measurements at the 12 WWTPs in the USA the emission of N₂O was in general higher from aerated zones than from non-aerated zones as can be seen from Figure 7 (note y-axis is logarithmic).

FIGURE 7 N₂O EMISSIONS FROM AEROBIC AND ANOXIC ZONES IN DIFFERENT WWTPS MEASURED AT HIGH (A) AND LOW (B) TEMPERATURES. SPECIFIC TEMPERATURES DESCRIBED IN TABLE 6. STEP-FEED BNR 3 IS NOT INCLUDED SINCE THE EMISSIONS FROM THE COVERED AEROBIC AND ANOXIC ZONES COULD NOT BE DISTINCTLY MEASURED



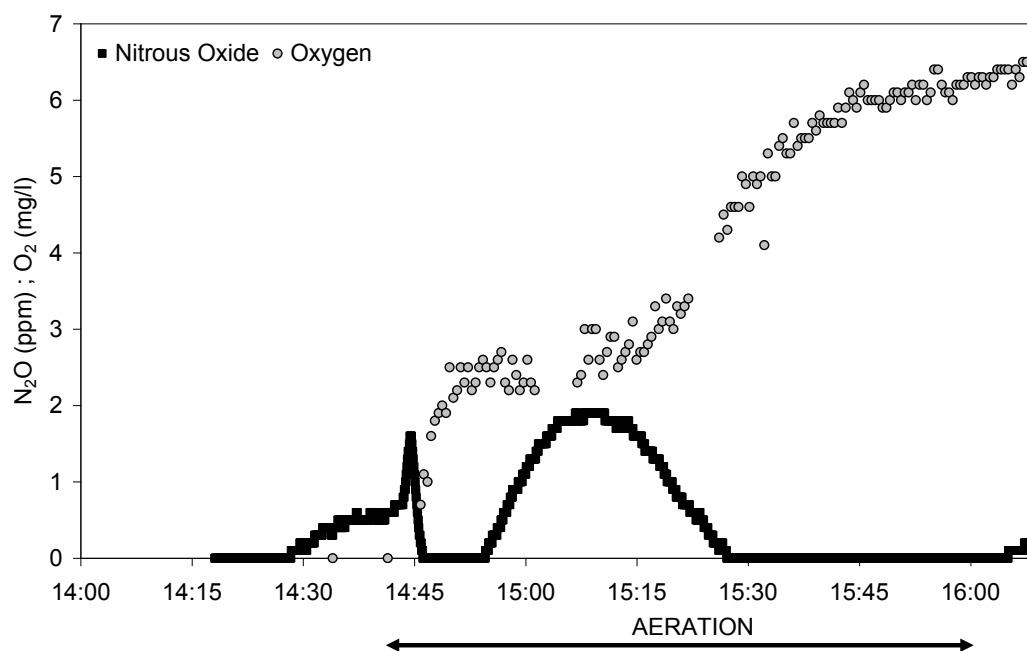
This indicates that the nitrification could be responsible for the formation of N₂O. However, based on these data the distinction between stripping of N₂O (from anoxic zones) or formation in the aerobic zone cannot be made. More information on this point can be obtained when measurements on liquid and gas phase N₂O are available per reactor zone. These measurements have been performed at different WWTPs in the USA. The results from one of them are presented in Table 7.

TABLE 7 SPATIAL PROFILE OF GASEOUS N₂O CONCENTRATIONS AND TYPICAL ACTIVATED SLUDGE VARIABLES IN A STEP-FEED BNR PROCESS SHOWING INDIVIDUAL SAMPLING LOCATIONS. RESULTS ARE FROM DISCRETE SAMPLING OVER A PERIOD OF 30 MINUTES AT EACH SAMPLING POINT. ARROWS INDICATE WASTEWATER FLOW. SHADED AND UNSHADED BOXES REPRESENT NON-AERATED AND AERATED ZONES, RESPECTIVELY. GASEOUS N₂O CONCENTRATIONS ARE EXPRESSED AS AVG. \pm SD. OF 30 MEASUREMENTS

Species	Anoxic →	Aerobic 1 →	Aerobic 2 →
NH ₄ ⁺ (mg-N/l)	14	12 \pm 5	1.5 \pm 0.71
NO ₂ ⁻ (mg-N/l)	0.00 \pm 0.00	0.00 \pm 0.00	0.00 \pm 0.00
NO ₃ ⁻ (mg-N/l)	0.85 \pm 0.10	2.7 \pm 0.35	10 \pm 0.21
DO (mg O ₂ /l)	0.10	2.3	4.2
Aqueous N ₂ O (μg/l)	55	190	570
Gaseous N ₂ O (ppmv)	1.5 \pm 0.14	16 \pm 0.27	23 \pm 0.67

In Table 7 there is a strong increase in N₂O concentration at the transition from the anoxic zone to the first aerobic zone. At this point it is thought that the nitrification was the main process that contributed to the N₂O formation, however the contribution of the denitrification cannot completely be excluded here. At the transition from the first aerobic zone to the second zone another strong increase in N₂O concentration can be observed, which is a strong indication that nitrification was responsible for the formation of N₂O. This observation is supported by a measurement in a complete stirred reactor (WWTP1; France) where the N₂O concentration in the gas phase was monitored before and after the start of the aeration. The results of these measurements are presented in Figure 11.

FIGURE 8 N₂O EMISSION DURING NITRIFICATION IN WWTP1 (FRANCE); DATE 06/2007



From Figure 8 it can be observed that a first peak of N₂O occurred at the start of the aeration, which is most likely formed earlier during denitrification. A second larger peak occurred during the aeration period. This indicates that the emitted N₂O is formed by nitrifying bacteria.

5.1.3 PROCESS PARAMETERS OF INFLUENCE

Knowledge on the process parameters that influence the formation and emission of N₂O can help to define measures to control the formation and emission of N₂O. Based on the results in the USA, multivariate regression modelling¹¹ was performed on all the collected data. This modelling was performed for both the aerobic and the anoxic zones.

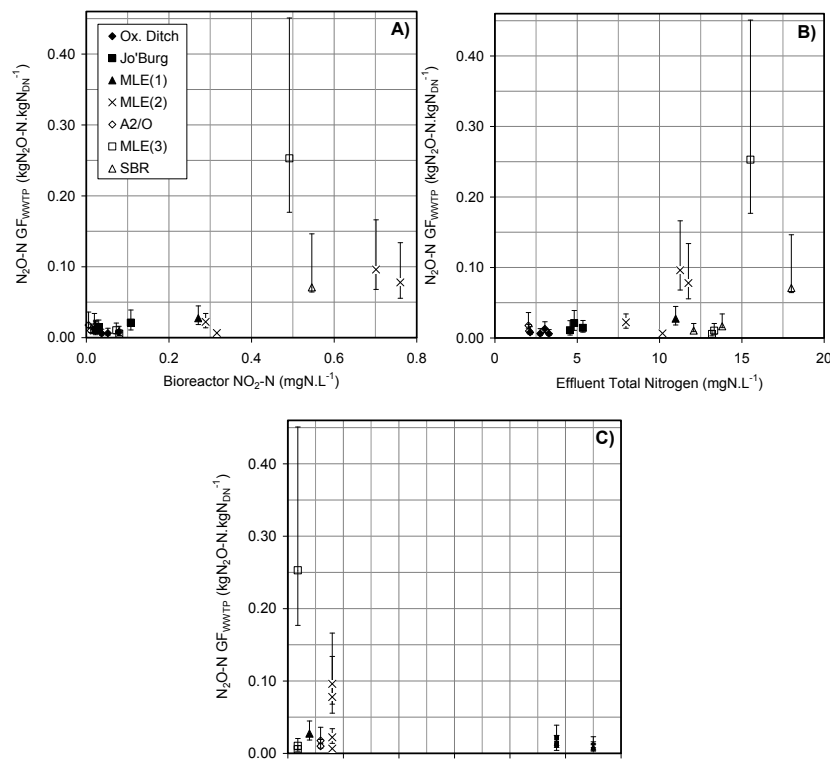
The factors that positively correlated with N₂O emissions from aerobic zones were NH₄⁺, NO₂⁻ and DO concentrations (isolated effect), and NH₄⁺ and NO₂⁻ concentrations (combined effect).

The factors that positively correlated with N₂O emissions from anoxic zones was the DO and NO₂-N concentration (combined effect).

The positive correlation between N₂O emission and the concentration of nitrite in the liquid phase, as found in the USA, is supported by the results found in Australia, as can be observed from Figure 9A. Although the number of data points is limited, there appears to be a threshold value at approximately 0.3 – 0.5 mg NO₂-N/l at which the generation factor increases sharply.

Figure 9 shows also the emission of N₂O as function of the effluent total nitrogen (B) and a-recycle rate (C). From these two last figures it can be observed that two WWTPs (Oxidation ditch and Johannesburg) have very high a-recycle rates¹² and correspondingly low effluent TN concentrations. These two WWTPs are also among those with the lowest N₂O emission, which indicates that the level of recirculation is a process parameter that influences the level of N₂O emission.

FIGURE 9 NET N₂O GENERATION FACTOR, GFWWTP, IN EACH SAMPLING ROUND, PLOTTED AGAINST A) BULK BIOREACTOR NITRITE-N CONCENTRATION, B) EFFLUENT TOTAL NITROGEN, AND C) A-RECYCLE RATE (AEROBIC ÷ ANOXIC) AS A MULTIPLE OF THE AVERAGE INFLUENT FLOWRATE, Q



11 Details on the used methodology and results can be found in Chandran, 2010.

12 Recycle between aerobic and anoxic zone, as a multiple of the average influent flowrate.

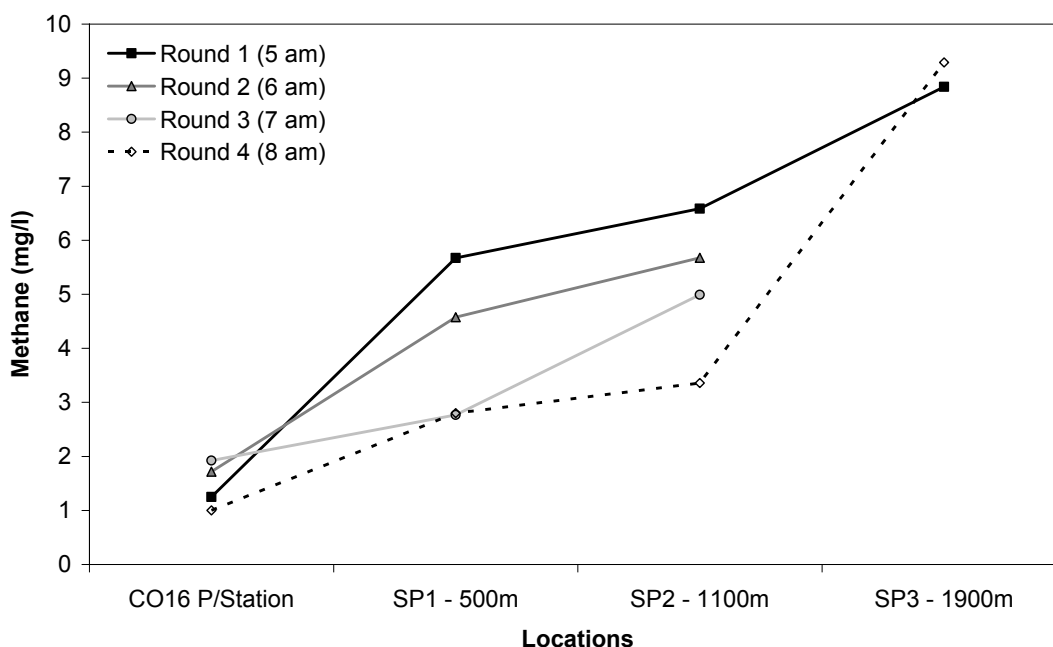
Although a large variation in N₂O emission was observed at the different temperatures (see Table 6) no correlation could be found between N₂O emission and temperature (based on multivariate regression modelling results USA).

5.2 CH₄ EMISSION FROM SEWERS

5.2.1 LIQUID PHASE

The results of one of the measuring campaigns at the CO16 raising main in Australia are presented in Figure 10.

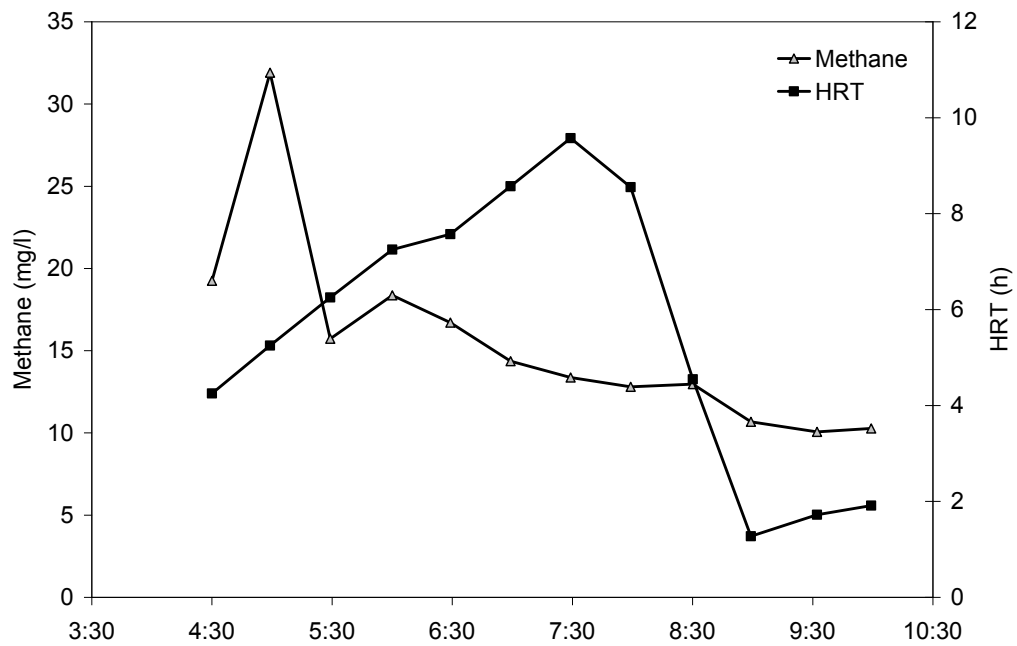
FIGURE 10 METHANE DATA MEASURED AT FOUR LOCATIONS ALONG CO16. THE AVERAGE WASTEWATER TEMPERATURE WAS 23.5°C (FOLEY ET AL., 2009)



From Figure 10 it can be observed that already some methane is present in the pumping station (1-2 mg/l), and that the concentration increased further downstream, reaching approximately 9.0 mg/l. Furthermore it can be observed that the methane concentration varied considerably with time at the 500m and 1100m locations, likely due to the variation of HRT of the wastewater samples collected. By taking all results together, the average methane production rate was calculated as 0.7 mg·l⁻¹·hr⁻¹ or in terms of sewer biofilm area 1.3 g·m⁻²·d⁻¹.

In another measuring campaign, the 1100m location was sampled half-hourly during 4:15 a.m. and 10:00 a.m. The results are presented in Figure 11.

FIGURE 11 METHANE DATA MEASURED AT C016 AT 1,100M IN ANOTHER CAMPAIGN. THE AVERAGE WASTEWATER TEMPERATURE WAS 22.5 °C



The methane concentrations measured in this measuring campaign were approximately three times higher than those presented in Figure 10. This difference could not be fully explained by the differences in HRT (4.0 – 9.5 hr in this case in comparison with 1.5 – 7.3 hr in first case). The average methane production rate was calculated as $3.1 \text{ mg} \cdot \text{l}^{-1} \cdot \text{hr}^{-1}$ or $5.5 \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, three times higher than the values obtained in the previous case. The average wastewater temperature was 22.5 °C, which was similar to that in the previous case. The reason for the much higher methane production in this case is not known. This could be related to the COD (Chemical Oxygen Demand) concentration, which was unfortunately not measured during either measurement campaign.

5.2.2 GAS PHASE

The results of the measuring campaigns at 64 (presented 59) lift stations in the USA are presented in Figure 12.

FIGURE 12 INSTANTANEOUS CH₄ READINGS DURING WINTER AND SUMMER MONITORING AT 59 LIFT STATIONS IN DEKALB COUNTY, GEORGIA, USA (NOTE X-AXIS IS LOGARITHMIC)

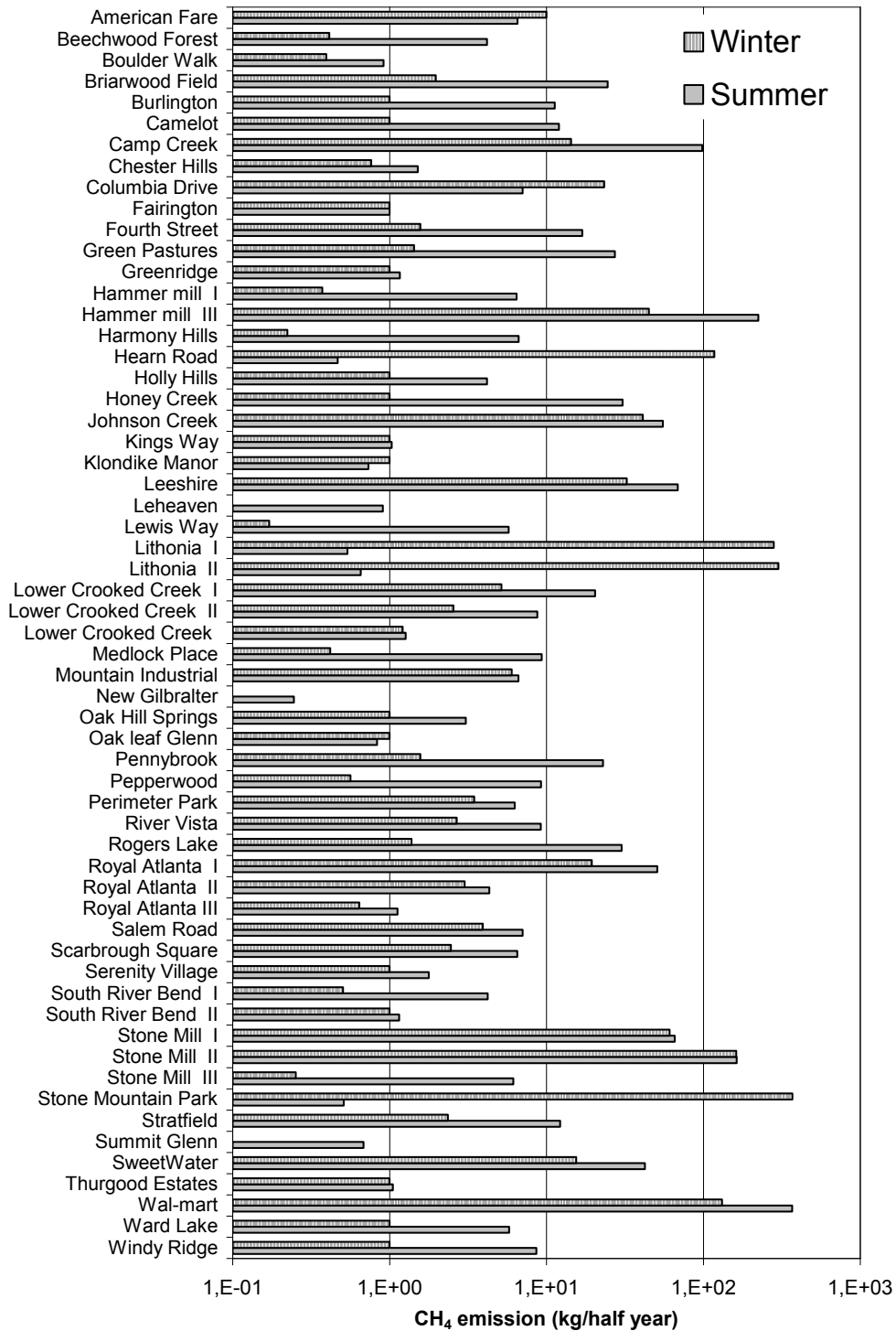


Figure 12 shows the calculated semi-annual mass emissions calculated from the winter and summer grab samples and the volumetric displacement of each station during each semi-annual period. Most of the summer emissions are higher than the winter emissions; likely because more methane is formed and methane solubility is less at higher temperatures.

5.2.3 MITIGATION STRATEGIES

The results of three mitigation strategies will be presented in this section, which are pH elevation, nitrite and iron salt addition.

PH ELEVATION

The effect of pH elevation on the VFA¹³ and methane production in a laboratory scale sewer reactor is presented in Figure 13.

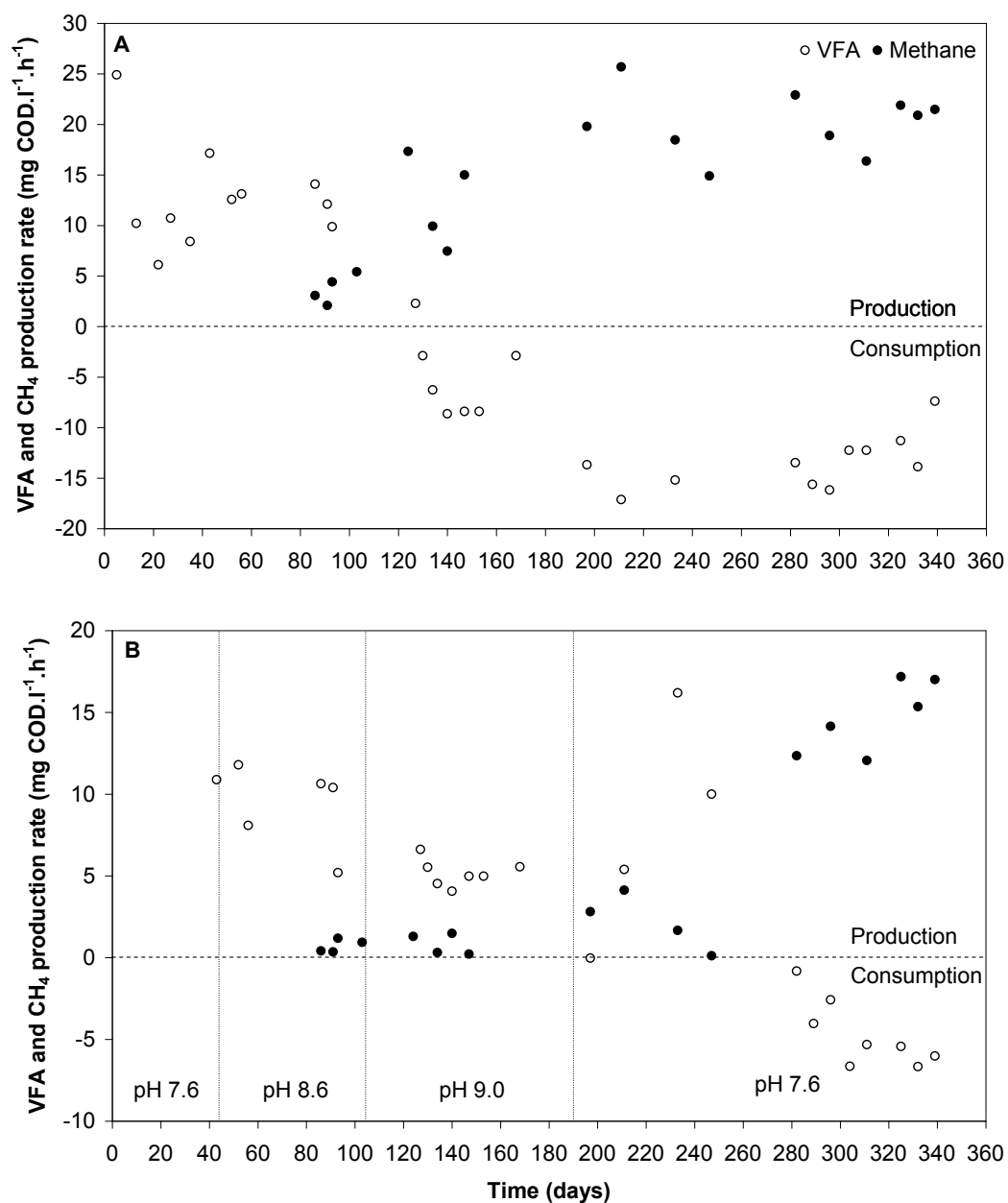
From Figure 13 it can be observed that methanogenic activities developed in the control reactor within three months after the reactor start-up, while no significant methanogenic activities were detected in the experimental reactor until normal pH was resumed. The results suggest that elevated pH at 8.6 - 9.0 suppressed the growth of methanogens.

Elevated pH conditions also reduced the activity of fermentative bacteria (FB) in the reactors. Prior to the development of the methanogenic activity, a stable VFA production rate of $11.5 \pm 1.2 \text{ mgVFA-COD} \cdot \text{l}^{-1} \cdot \text{hr}^{-1}$ was observed in the control and experimental reactors. The FB activity decreased to $5.1 \pm 0.4 \text{ mgVFA-COD} \cdot \text{l}^{-1} \cdot \text{hr}^{-1}$ in the experimental reactor under pH 9.0 (with negligible methane formation). This indicates that the fermentation activity was reduced by 54% at pH 9.0 in comparison to pH 7.6.

Furthermore, it was observed that the activity of sulphate reducing bacteria was reduced by 30 – 50% respectively at pH 8.6 and pH 9.0. The results further showed that pH elevation not only reduced the H₂S transfer but also its production by sewer biofilms. When normal pH was resumed, it took approximately 2 months for the SRB (sulphate reducing bacteria) activity to fully recover (Gutierrez et al., 2009).

13 Volatile fatty acids.

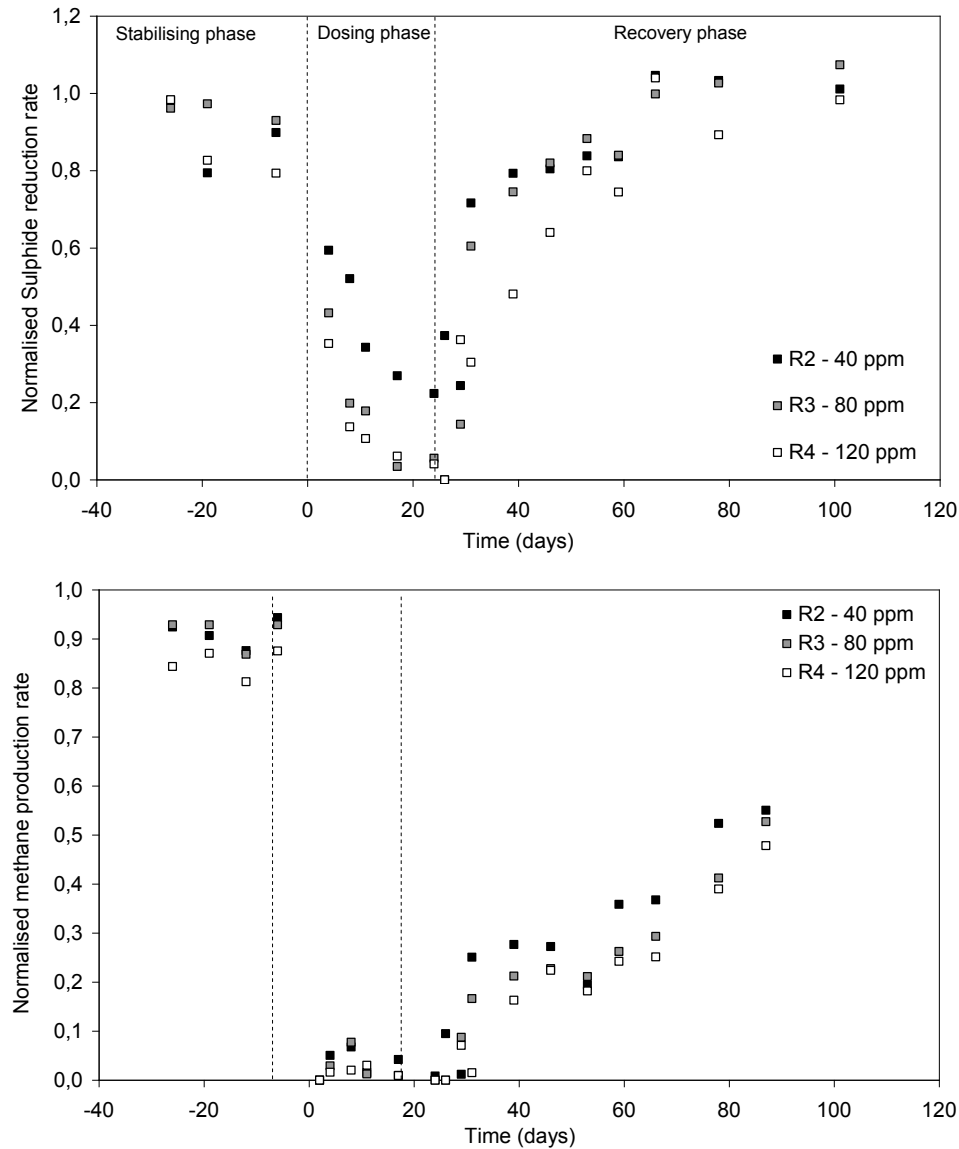
FIGURE 13 EVOLUTION OF THE VFA (○) AND METHANE PRODUCTION RATES (●) IN THE CONTROL (A) AND EXPERIMENTAL (B) REACTORS. NOTE THAT METHANE PRODUCTION RATES HAVE A UNIT OF $\text{MGCOD}\cdot\text{L}^{-1}\cdot\text{HR}^{-1}$ IN THIS FIGURE, RATHER THAN $\text{MGCH}_4\cdot\text{L}^{-1}\cdot\text{HR}^{-1}$, FOR DIRECT COMPARISON WITH THE VFA PRODUCTION/CONSUMPTION RATES. $1 \text{ MGCH}_4 = 4 \text{ MGCOD}$



NITRITE ADDITION

The impact of nitrite addition on the methanogenic and sulphate reducing activities were studied on both laboratory-, and full scale. The results of the laboratory experiments are presented in Figure 14.

FIGURE 14 NORMALIZED METHANE PRODUCTION RATE IN NITRITE-DOSED REACTORS: R2 (\blacksquare), R3 (\square), AND R4 (\triangle), RELATIVE TO THE CONTROL REACTOR R1 (I.E. THE ACTIVITY MEASURED FOR R1 ON EACH MEASUREMENT DAY WAS CONSIDERED 100%, TO ELIMINATE THE RATE VARIATION CAUSED BY CHANGES IN WASTEWATER QUALITY). NITRITE ADDITION WAS INITIATED ON DAY 0 AND FINISHED ON DAY 24



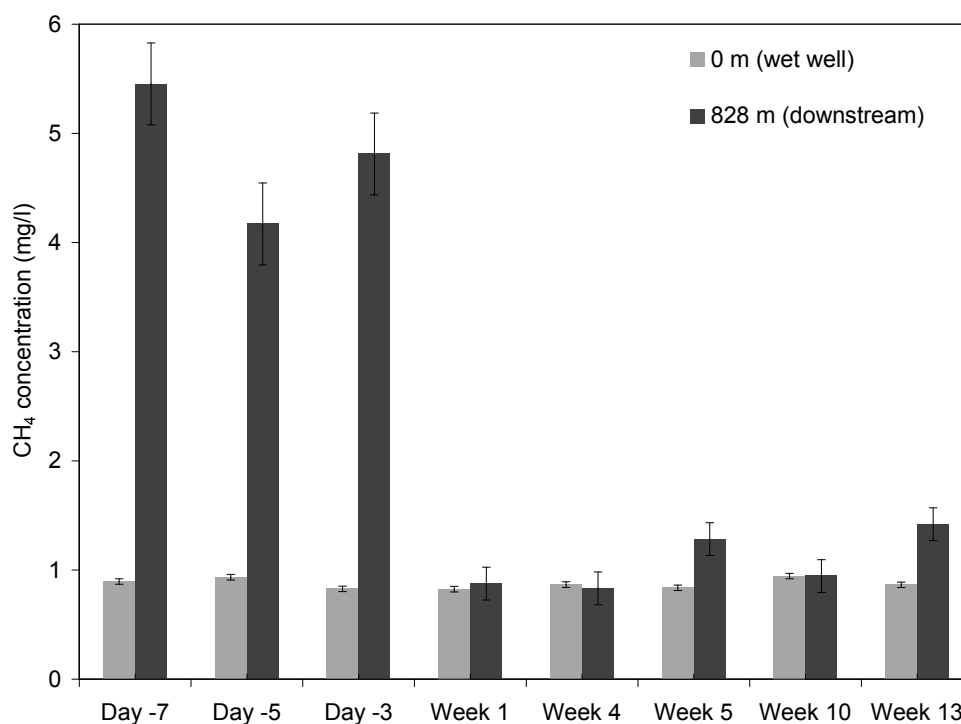
From Figure 14 it can be observed that:

- The methane¹⁴ production in dosed reactors was reduced to negligible levels within two days after the initiation of nitrite dosage.
- The different levels of nitrite addition did not cause any difference in inhibition.
- Complete methanogenic inhibition was achieved with the lowest nitrite concentration used in the experiment, i.e. 40 mg-N/l
- The recovery of methane production proceeded at very similar rates in all cases.
- The recovery process was almost linear during the whole recovery phase.
- Only less than 60% of recovery was achieved after two-month of recovery.
- Suppression of the sulphide production was also achieved with nitrite dosage at 80 mg-N/l and 120 mg-N/l.
- The recovery of the sulphide production was faster than the recovery of the methane production.

14 The methanogenic activity was measured in the absence of nitrite through batch tests using fresh sewage without nitrite addition in all cases.

The results of the field trial at the real sewer line UC09 are presented in Figure 15, which shows the concentrations of methane in the wet well (0m) and at the point 828m downstream.

FIGURE 15 DAILY AVERAGE METHANE CONCENTRATION AT 828M AND AT THE PUMPING STATION WET WELL. DAY -7, -5, AND -3 WERE DURING THE BASELINE PERIOD. NITRITE WAS ADDED INTERMITTENTLY AT 100 MGN/L DURING DAY 0 – 2 FOR A TOTAL DOSING TIME OF 33 HOURS OVER A 3-DAY PERIOD. WEEK 1 TO 13 IMPLY 1 – 13 WEEKS AFTER THE DOSAGE. METHANE CONCENTRATIONS WERE BASED ON MANUAL SAMPLING AND OFFLINE MEASUREMENTS (3 – 6 SAMPLES WERE TAKEN ON EACH SAMPLING DAY). THE ERROR BARS SHOWN ARE STANDARD ERRORS (N = 3 – 6)



Complete suppression of methane production by nitrite addition was observed, as indicated by the nearly identical methane concentrations in the pumping station and at 828 m. One month after terminating nitrite dosage, methane concentration at 828m remained at a level similar to that measured in the wet well, indicating that the sewer biofilm ceased to produce methane in this period. The activity increased only marginally in the following two months.

In general, the field trial confirmed the results of the laboratory study, that nitrite has a long-term toxic effect on methanogens (and sulphate reducing bacteria – data not shown) in anaerobic sewer biofilms. Both the field and laboratory results collectively suggest that nitrite could be applied intermittently to achieve sulphide and methane control in sewers.

IRON SALT ADDITION

In the experiments where iron salts were added to laboratory scale rising main sewer systems, Fe³⁺ dosage was found to significantly inhibit (next to precipitation with sulphide) sulphate reduction and methane production by sewer biofilms. The sulphate reduction rate was found to be inhibited by 40 – 60%, while the methanogenic activity was inhibited by 50 – 80%. The rate data were supported by significantly lower methane concentrations at the end of the experimental rising main system (Zhang et al., 2009). The mechanisms responsible for the inhibition observed are yet to be fully understood.

5.3 CH₄ EMISSION FROM WWTPS

5.3.1 EMISSION OF CH₄

The emission of CH₄ as reported at the four WWTPs in France and the three WWTPs in the Netherlands are presented in Table 8.

TABLE 8 EMISSION OF CH₄ FROM WWTPS IN FRANCE AND THE NETHERLANDS

Country	WWTP	Emission (kgCH ₄ /kgCOD _{influent})	Emission (kg CH ₄ -COD/kg COD _{influent})
France	WWTP 1	< 0.0001	< 0.0004
	WWTP 2	< 0.0001	< 0.0004
	WWTP 3	0.0004	0.0016
	WWTP 4	0.0003	0.0012
The Netherlands	Papendrecht	0.0087	0.035
	Kortenoord	0.0053	0.021
	Kralingseveer October	0.012	0.048
	Kralingseveer February	0.008	0.032

Based on Table 8 the following observations can be made:

- The highest emission of methane occurred at WWTP Kralingseveer in October. This could be related to the presence of a sludge digester at this WWTP where at Papendrecht and Kortenoord a sludge digester is absent.
- In February the emission at Kralingseveer was lower than in October. This could be related to the temperature of the water which was 19°C in October and around 10 °C in February. At lower temperatures less methane will (probably) be produced and more methane will be dissolved. For this reason methane could have left the WWTP via sludge or the effluent. However, the concentration of soluble methane in both streams was not determined.
- The emission factors for CH₄ differed (in some case higher; in other cases lower) than the emission factor¹⁵ currently used in the Netherlands to estimate the emission of CH₄ from WWTPs.

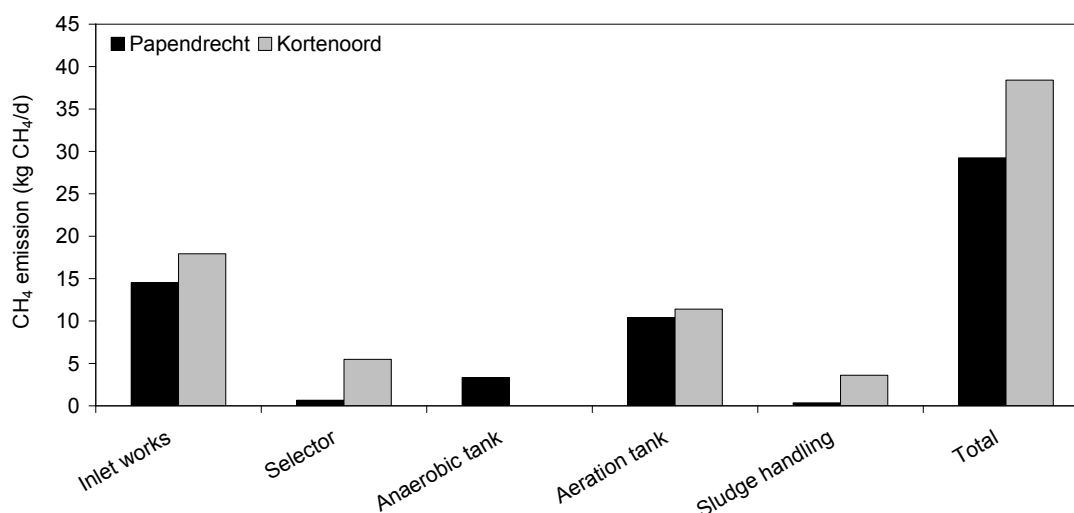
5.3.2 ORIGIN OF EMISSION

At the three WWTPs in the Netherlands, the total CH₄ emission was determined based on grab samples from all present process parts. In this way the origin of the methane emission could be determined. The results for the two WWTPs without sludge digestion are presented in Figure 16.

The emission of CH₄ at the two WWTPs primarily occurred from the inlet works and the aeration tanks. The contribution of the sludge handling sites was minimal. In both cases, the contribution from the inlet works formed almost half of the total CH₄ emission. The contribution from the aeration tank was 36% in Papendrecht and 30% in Kortenoord. It should be noted that some of the CH₄ emitted at a WWTP could have originated from sewers. CH₄ formed and subsequently transported to the treatment plants can be stripped at the inlet works and the subsequent process units.

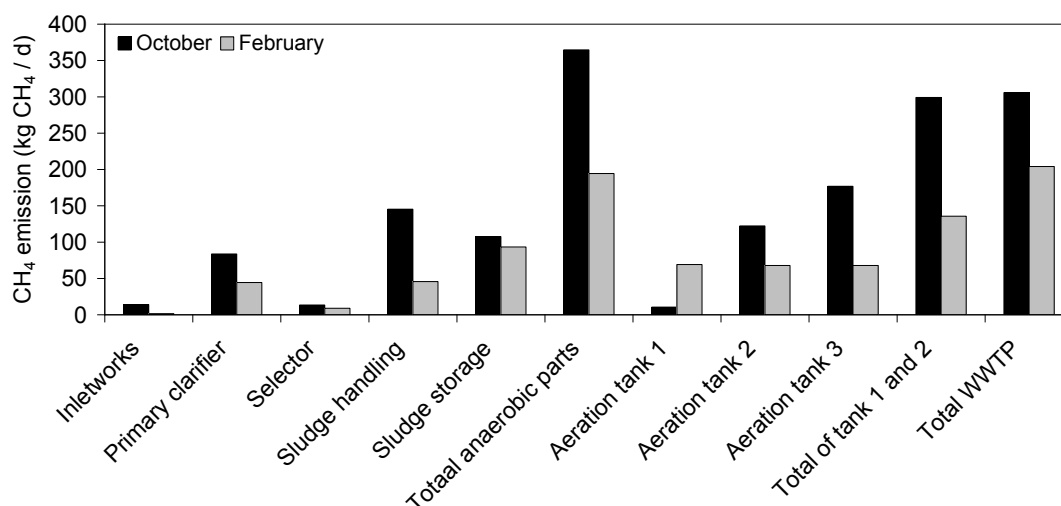
¹⁵ For the national inventory reports 0.007 kg CH₄/kg COD_{influent} are used for WWTPs without sludge digestion and 0.0085 kg CH₄/kg COD_{influent} for WWTPs with sludge digestion (VROM, 2008).

FIGURE 16 ORIGIN OF METHANE EMISSION AT THE WWTPS IN PAPENDRECHT AND KORTENOORD



For both measurement periods at Kralingseveer the origin of the CH₄ emission is presented in Figure 17.

At WWTP Kralingseveer the ventilated air from all anaerobic parts is treated separately in a compost filter. After this treatment, the air is reused in the aeration tanks 1 and 2. For this reason the total CH₄ emission after the anaerobic parts is presented as well in Figure 17.

FIGURE 17 OVERVIEW OF THE CH₄ EMISSION AT WWTP KRALINGSEVEER DURING THE MEASUREMENT CAMPAIGN IN OCTOBER (2008) AND FEBRUARY (2009)

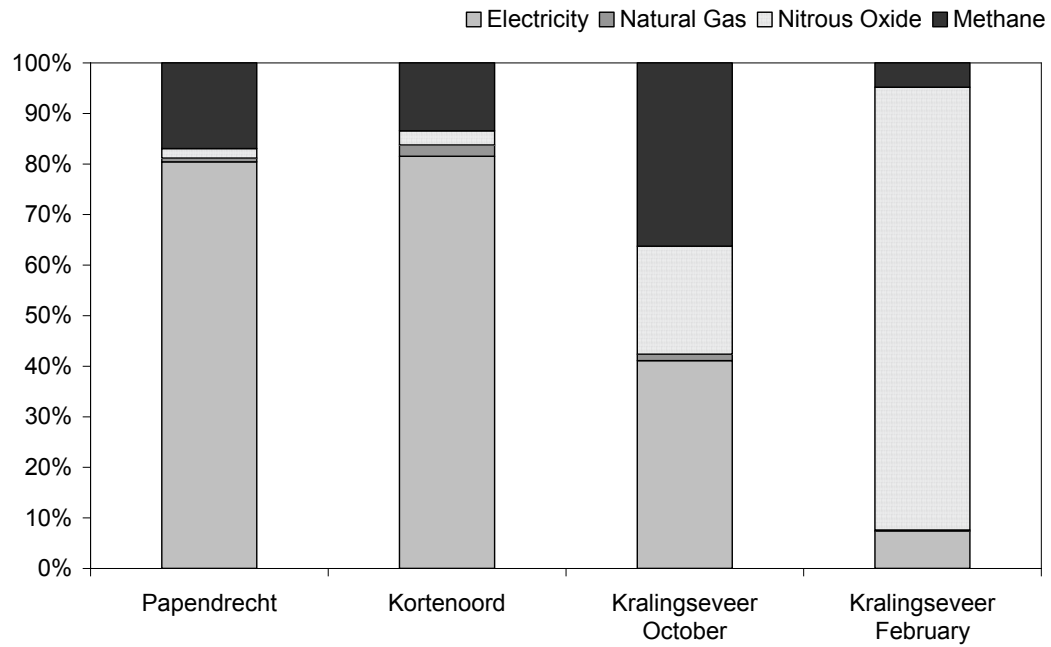
From Figure 17 it can be observed that the emission of CH₄ from all anaerobic parts is larger than the total CH₄ emission from aeration tanks 1 and 2. This implies that some CH₄ is lost or converted during treatment in the compost filter or in the old aeration tanks. The loss of CH₄ in October was 92 kg CH₄/d and for February the loss was 59 kg CH₄/d.

The main parts that contributed to the emission of CH₄ were the primary clarifier, the sludge handling and storage units. The contribution of the primary clarifier was 23% in both periods. For the sludge handling the contribution was 45% in October and 23% in February. Finally the sludge storage contributed 28% in October and 48% in February.

5.4 TOTAL CARBON FOOTPRINT

The contribution of each greenhouse gas to the total carbon footprint of the three WWTPs from the Netherlands is presented in Figure 18.

FIGURE 18 TOTAL CARBON FOOTPRINT OF WWTP KORTENOORD (A; THE NETHERLANDS) AND WWTP KRALINGSEVEER OCTOBER (B; THE NETHERLANDS)



From Figure 18 it can be observed that:

- Electricity forms the major contributor to the total carbon footprint at WWTPs with a low N-sludge load (Papendrecht and Kortenoord).
- At the WWTP (Kralingseveer) with a higher N-sludge load the contribution of N₂O can be substantial.
- The contribution of CH₄ to the total carbon footprint depends on the presence of a sludge digester. In the last case (Kralingseveer) the contribution of CH₄ can be substantial.

6

DISCUSSION

6.1 METHODOLOGY

6.1.1 N₂O EMISSION

The research presented in this report used different methodologies to determine the emission of N₂O from WWTPs. The weak and strong points of these monitoring technologies are summarised in Table 9.

TABLE 9 STRONG AND WEAK POINTS METHODOLOGIES TO DETERMINE N₂O EMISSION FROM WWTPS REGARDING VARIABILITY AND ORIGIN
(+ REFERS TO BE SUITABLE, +/- REFERS TO BE LESS SUITABLE, - REFERS TO BE NOT SUITABLE)

Methodology	Variability	Origin / process parameters of influence
Liquid phase measurements / mass balance (Australia)	-	+
Gas hood (France / USA)	+/-	+
Gas phase covered WWTPs (The Netherlands)	+	+/-

To determine the N₂O emission from uncovered WWTPs different methodologies were developed. In Australia a method was developed based on liquid phase measurements for individual reactor zones. Based on mass transfer coefficients a complete mass balance over the different zones and the complete WWTP could be made. In this way the emission of N₂O was determined, but it was also possible to differentiate between N₂O emission and generation. However, this method does not allow for sufficient insight in the variation of N₂O emission as the method is based on grab samples.

The methodologies developed in the USA and France were based on gas hoods measurements. Those gas hoods were placed at the different zones of a WWTP and in case of the USA, the gas hoods measurements were combined with liquid phase measurements. By placing the gas hoods at the different zones of a WWTP and combine those with the liquid phase measurement it was also in the USA possible to differentiate between N₂O emission and generation. On the other hand, the gas-hood measurements are limited by the dimensions of the hood itself. Additionally, heterogeneities in the emission gas flow rate could also contribute to the variability in the actual emissions, which needs to be considered. To calculate the total emissions load from a plant, both the N₂O concentrations and advective gas flow must linearly be scaled up from the hoods to the entire activated sludge bioreactor. Alternately, multiple measurements need to be done at different locations in the activated sludge reactor to capture the spatial variability in emissions.

The methodology used in the Netherlands was based on the analyses of the total off gas of covered WWTPs. The advantage of this method is that it captures the total emissions given the variability of N₂O emission in time and space, but with this methodology it is more difficult to differentiate between N₂O emission and generation.

To finally estimate and control the emission of N₂O from WWTPs, the use of all available methods will be required.

6.1.2 CH₄ EMISSION

In the research performed in Australia, no CH₄ emission data were calculated. In the USA, the emission of methane was calculated from unventilated lift stations. For this gas flow needed to be determined. This was done via the active volume of each lift station in combination with the pumping rate of each of the pumps. It is hereby assumed that the amount of air breathed in and exhausted out during each pumping cycle is approximately equal to the active volume inside the wet well or the volume of raw sewage pumped during each cycle. However, the methodology used to determine the gas flow is subject to a number of limitations, namely:

- Dispersion of CH₄, which is lighter than air, is not accounted for. Many stations cycle only a few times per day and those stations likely lose a considerable portion of the evolved CH₄ to the atmosphere in between cycles. This phenomenon would result in under-reporting of actual emissions.
- Dispersion effects can be very significant at some of the larger pumping stations, like LCC-3. LCC-3 has a large, uncovered forebay with significant interchanges of outside air. On calm days the forebay air changes could be 1 to 5 times per hour and could increase to as much as 10 or 30 times per hour on windy days. This limitation, combined with the fact that these stations have the highest volume and mass throughput which should produce more CH₄, could represent a very significant source for under-reporting.
- During a pumping cycle, a significant volume of outside air is drawn into the wet well. If a sampling event occurred soon after such a dilution, the applied concentrations could under-report the actual CH₄ emissions.

These limitations show that there is a need for a good strategy to measure loads of methane emitted to the air from sewerage systems.

6.2 N₂O EMISSION

6.2.1 EMISSION

The results on the emission of N₂O from WWTPs showed that there exists a great variability among different WWTPs and at the same WWTP during different seasons or throughout the day. This great variability results from the fact that the formation of N₂O is very complex and can be executed by both autotrophic and heterotrophic bacteria. Those bacteria show a dynamic response to changing influent loads and process conditions resulting in a variable formation of N₂O in time and place. Because of the observed variability in N₂O emission the use of a generic emission factor to estimate the emission from a specific WWTP is inadequate. To determine the emission of N₂O from a specific WWTP measurements are required.

6.2.2 ORIGIN

N₂O can originate from denitrification and nitrification processes. Although the general assumption was that denitrification is likely the major source, the measurements and also several associated laboratory studies (e.g. Burgess et al., 2002) indicate that likely nitrification is a more important source of N₂O in the wastewater treatment plants.

This is observed from measured higher liquid N₂O levels in aerated zones compared to anoxic zones (see Table 7). Also when anoxic sludge gets aerated observations generally showed an initial sharp peak of N₂O emission likely due to stripping, whereas later a much higher amount of N₂O is emitted likely due to N₂O formation and stripping (see Figure 8).

6.2.3 PROCESS PARAMETERS INFLUENCE

Nitrite was measured in the USA plants; there it showed a strong correlation with N₂O emission. The results from Australia supported these findings as could be observed from Figure 9A.

The stimulating effect of nitrite (especially at low concentrations 0-2 mgN/l) has also been shown by several laboratory investigations (e.g. Tallec, 2006). Therefore it is likely that all factors (lower DO, sudden changes in ammonium load) that lead to nitrite build up in a treatment plant will also enhance N₂O emissions.

Ammonium is a substrate for N₂O formation by nitrifying bacteria. The correlation found in the US study between ammonium levels and N₂O emission is in accordance with this fact and the theory that N₂O is mainly derived from nitrification. The observations of correlations between daily variations in ammonium load and N₂O emission are in line with ammonium substrate utilization but are also in line with laboratory results showing that when nitrifying bacteria increase their nitrification rates they produce N₂O (Yu et al., 2010).

For other factors (e.g. COD availability) reported in literature to have a potential impact on N₂O emissions were not supported by direct observations that they are important. Given the level of knowledge, however, it should not be concluded that such factors do not play a role.

6.2.4 IMPLICATIONS OF GAINED KNOWLEDGE

Based on the above, it becomes clear that the formation of N₂O increases in aerobic zones at increasing levels of NH₄⁺, NO₂⁻ and DO (but also at low levels).. This implies that if high concentrations of these constituents can be avoided in practice, the risk of N₂O emission will be reduced. These high concentrations can be avoided in:

- systems that approach “ideal” well-mixed conditions (i.e. high recycle rates). In this way concentrations of intermediates from nitrification-denitrification including NO₂-N and NO are diluted, thereby reducing their inhibitory effect (Casey et al., 1999a,b). This is confirmed by the general results from all studies that WWTPs with the highest recycle rates and with the lowest TN effluent concentrations belonged to the WWTPs with the lowest N₂O emission.
- systems that avoid over – aeration i.e. have a rapidly responding DO control systems. In this way high levels of DO in aerobic and anoxic zones can be avoided
- systems that are equipped with flow equalization. Such systems minimize the peaking factor of influent nitrogen (ammonium) loading to the activated sludge system.

With the presented insight, it has been possible to estimate the risk of N₂O emissions from a specific WWTP based on the risk matrix presented in Table 10.

TABLE 10

RISK MATRIX TO DETERMINE RISK LEVEL OF N₂O EMISSION

Risk on N ₂ O	High	Medium	Low
Parameter			
Effluent total nitrogen (mg/l)	> 10	5 - 10	< 5
Range in N-concentration in plant	H	M	L
Load variations	H	M	L
Maximum nitrite concentrations anywhere in plant	> 0.5*	0.2 – 0.5	0.2

* Risk does not increase at nitrite concentrations higher than 2 mg N₂O-N/l.

In summary, it can be concluded that in systems with extensive nitrogen removal the formation of N₂O is highly minimized. In other words, there is no conflict between water quality and air quality; rather they go hand in hand. This implies that systems that are not designed for (complete) nitrogen removal exhibit a high risk of N₂O emission. At temperatures of 20 °C, an aerobic SRT of 2-3 days is already sufficient to get nitrification. In these high-loaded systems, nitrite easily accumulates resulting in greater N₂O formation.

6.2.5 FUTURE RESEARCH

The results of the presented research from Australia, France, the USA and the Netherlands already clearly identified key process parameters that influence the emission of N₂O from WWTPs. This knowledge presents a good starting point for defining mitigation strategies to reduce the emission of N₂O. Future research should first give better insight into the variability of N₂O emissions over prolonged times in order to develop proper sampling protocols for emissions of N₂O from treatment plants. A better understanding of the processes leading to nitrite formation in treatment plants can lead to mitigation strategies for N₂O emissions. Besides activated sludge systems, biofilm processes should be monitored for potential emissions. A better insight in N₂O production in natural systems can improve decisions on implementing full nitrogen removal as a mitigation strategy for N₂O emissions from treatment systems as well as natural systems.

6.3 CH₄ EMISSION

6.3.1 SEWERS

The measurements performed in Australia and the USA show that substantial amounts of methane can be formed and emitted from sewer systems. In addition to this, substantial amounts of methane were measured from the inlet works at the WWTPs in the Netherlands. With this knowledge, the contribution of the sewer system cannot be neglected as assumed in the current IPCC guidelines (IPCC 2006a). However, to be able to make a good estimate of the contribution of sewers to the total CH₄ emission from wastewater collection and treatment systems more data are required and a good strategy to measure methane loads is necessary (refer to section 6.1.2). The data collected to date are far from adequate for the development of reliable accounting guidelines, and for the development, calibration and validation of CH₄ emission models. It is of utmost importance that such data are collected from sewer networks (rising mains, and gravity sewers) around the world under different climate conditions, and from networks collecting and conveying various types of wastewaters. Both liquid and gas phase data are urgently needed.

The results from the lift stations (fed mostly by gravity sewers) in the USA (Figure 12) showed that the concentration of methane in the gas phase was in almost all cases (80%) higher in summer than in winter. This indicates that temperature is an important parameter determining the formation of methane in sewers. This might also explain relative high methane levels in Australia, although this could also result from differences in the composition of wastewater.

6.3.2 MITIGATION STRATEGIES

Several strategies used for sulphide control in sewers have been found to reduce methane formation (Figure 13 - Figure 15). However these strategies may not be the most cost-effective methods for methane control. Given the high sensitivity of methanogens to environmental changes, more cost-effective strategies may be developed. The addition of nitrite is a very promising technology in this respect, but might easily lead to N₂O formation.

6.3.3 WWTPS

Based on the measurement in the Netherlands methane emission at a WWTP seems to originate from two major sources. First the sewer seems to be a major source as a high methane emission was observed from the inlet works and the aeration tanks. The second major source seems to be related to the sludge digester as high emissions of methane were observed from sludge handling facilities related to the sludge digester. These are the facilities that store the digested sludge before and after the dewatering facilities. In these facilities the methanation is still progressing, and methane dissolved in the liquid will be stripped. The methane that is formed inside the sludge digestion tank is combusted in combined heat power equipment, and it is thought that the leakage of CH₄ is minor.

For the storage facilities technological and technical adaptations will have to be developed in order to minimise the emissions of methane. Also the potential to have the methane biologically oxidised before it is stripped will have to be investigated.

From the results at the WWTP it is shown that process units that are known for their sulphur related odours (inlet works, sludge digesters) also emit methane.

6.4 TOTAL CARBON FOOTPRINT WWTP

As a first indication on the possible contribution of N₂O and CH₄ emission to the total carbon footprint of a WWTP, the result in the Netherlands could be used as an example.

In the case studies in the Netherlands, the specific emissions of N₂O and CH₄ were determined at the same time. Together with the data on the related consumption of electricity and natural gas, it was possible to calculate a carbon footprint of three WWTPs. To determine the carbon footprint, all sources were converted to CO₂ equivalents¹⁶. The results in the Netherlands indicated that the emission of CH₄ and N₂O can significantly contribute to the total carbon footprint of a WWTP. This contribution can vary from 2% to almost 90% of the carbon footprint under extreme conditions for N₂O and 5 – 40% for CH₄. One should be aware that these numbers are specific for the Netherlands. In any other country, these numbers can differ greatly as there exist a great variation in the way wastewater and sludge is handled as well as the specific composition of the energy mix used. Furthermore these numbers can significantly differ depending on how the boundaries are set around the analysis. In case of the analysis performed for the three Dutch WWTPs the contribution of e.g. chemical use, and sludge incineration were not accounted for.

¹⁶ It should be noted that the conversion numbers are country specific and do depend on the used energy mix (i.e. brown coal versus wind or solar energy), which is of influence on the total carbon footprint of a WWTP.

7

CONCLUSIONS AND FUTURE RESEARCH

7.1 CONCLUSIONS

7.1.1 N₂O EMISSION

Based on the research presented in this report the following conclusions can be drawn:

- The emission of N₂O is highly variable. For this reason the use of generic emission factors to estimate the emission from a specific WWTP is inadequate.
- To determine the emission of a specific WWTP, measurements are required. These measurements should be performed with online monitors and over the operational range of the WWTP.
- Emission of N₂O originates mainly from nitrification.
- Accumulation of nitrite leads to the formation of N₂O in mainly in aerobic zones.
- High NH₄ concentrations can lead to the emission of N₂O if nitrification occurs.
- The risk level of N₂O emission can be determined based on the following risk matrix:

TABLE 11

RISK MATRIX TO DETERMINE RISK LEVEL OF N₂O EMISSION

Parameter	Risk on N ₂ O		
	High	Medium	Low
Effluent total nitrogen (mg/l)	> 10	5 - 10	< 5
Range in N-concentration in plant	H	M	L
Load variations (daily)	H	M	L
Maximum NO ₂ concentration (mg N/l) anywhere in plant	> 0.5*	0.2 – 0.5	0.2

* Risk does not increase at higher NO₂ concentrations

- A good effluent quality (TN < 5 mgN/l) goes hand in hand with a low risk of N₂O emission.
- Non-BNR systems with unintentional nitrification will have a high risk of N₂O emission.

7.1.2 CH₄ EMISSION

Based on the research presented in this report the following conclusions can be drawn:

- Formation and emission of CH₄ from sewers can be substantial.
- Sulphur related odours are good indicators for methane formation.
- Odour mitigation strategies in sewers likely also support a reduced methane formation.
- Methane emission from WWTPs mainly originates from sewers and sludge handling.

7.1.3 TOTAL CARBON FOOTPRINT

- Emissions of CH₄ and N₂O can significantly contribute to the total greenhouse gas footprint of WWTPs as was seen from the results obtained in the Netherlands, but this can be different in other countries.

7.2 FUTURE RESEARCH

Based on the outcomes of the research valuable knowledge is gained to estimate and reduce the emission of N₂O and CH₄ from wastewater collection and treatment systems. Future applied research should focus on:

N₂O

- Variability of N₂O emission such that proper sampling and monitoring programmes can be developed.
- Mitigation strategies (including insight in the relative contribution of autotrophic and heterotrophic processes to N₂O generation) to reduce emission via process design and control;
- Evaluate emission from biofilm based processes;
- Evaluate emission from various receiving aquatic environments.

CH₄

- Development of a strategy to measure loads emitted from sewers;
- Build a database for emission measurements from sewers;
- Cost effective mitigation strategies¹⁷
- Emission from sludge treatment lagoons.

¹⁷ The addition of nitrite seemed to be a strategy that could reduce the formation of methane, however, given that nitrite is one of the factors that correlate with N₂O production, the impact of upstream nitrite addition and dosages on the potential on downstream N₂O emissions needs to be determined as well.

8

ACKNOWLEDGEMENTS

8.1 AUSTRALIA METHANE RESEARCH

The following people from the Advanced Water Management Centre at The University of Queensland are thankfully acknowledged for conducting the original research reported in this document on the measurement, understanding, modeling and mitigation of methane formation in sewers: David de Haas, Jeff Foley, Albert Guisasola, Oriol Gutierrez, Guangming Jiang, Jurg Keller, Paul Lant, Janani Mohanakrishnan, Keshab Sharma, Gatut Sudarjanto and Lishan Zhang.

The Australian Research Council (ARC), the Water Services Association of Australia (WSAA) and numerous members of the Australian water industry provided financial support to the research presented in this report through ARC projects LP0454182, ARC LP0882016 (<http://www.score.org.au/>) and the WSAA project Direct Methane and Nitrous Oxide emissions from full-scale wastewater treatment systems.

Dr Trisha Ibrahim from South East Water Limited (SEWL) kindly provided gas-phase methane data measured at one of the sewer lines operated by SEWL. The discussion with Trisha about these results has been very highly valuable.

Mr Shaun Corrie and Mr Ian Johnston from Allconnex Water (formerly Gold Coast Water) assisted with the collection of dissolved methane data from UC09 and CO16. They also provided on-line gas phase methane data measured at CO16.

8.2 AUSTRALIA NITROUS OXIDE RESEARCH

This work was funded by the Water Services Association of Australia and The University of Queensland. In-kind support was also provided by United Water International (Adelaide), and the participating water authorities.

The members of the project team for this study were:

Principal authors:	Jeff Foley (PhD student, UQ) Professor Paul Lant (UQ)
Fieldwork assistants:	Bill Fuller (Engineer, United Water International) Peter Muller (Undergraduate engineer, GHD) Con Foley (volunteer) Lyndon Clark and Debbie Chua (Water Corporation) Ian Johnson (Gold Coast Water)
Analytical and modelling support:	Dr Ursula Werner (UQ) Shihu Hu (PhD student, UQ) Dr David de Haas (UQ, GHD) Dr Keshab Sharma (UQ) Dr Albert Guisasola (Universitat Autònoma de Barcelona) Dr Beatrice Keller-Lehmann and Jianguang Li (UQ) Peng Su and Associate Professor Wei Zhang (Flinders University)
Technical review and stewardship:	Professor Zhiguo Yuan (UQ) Professor Jurg Keller (UQ) Dr David de Haas (UQ, GHD) Dr Paul Rasmussen (United Water International) Hamish Reid (South East Water) Michael Greg and Daniel Starrenburg (Brisbane City Council) Greg Allen (Sydney Water) Keith Cadee (Water Corporation) Adam Lovell (Science and Sustainability Manager, WSAA)

The authors also thank the plant owners and operators for their cooperation:

Brisbane City Council	Keith Barr, Vijay Jayaraman, Kenny Liew and Grahame Simpson
Fosters Brewery	Charlie Foxall
Gold Coast Water	Shaun Corrie, Ian Johnson and Kelly O'Halloran
Melbourne Water	Kim Daire, Peter Gall, Trevor Gulovsen, Suelin Haynes and Erik Ligtermoet
SA Water / United Water	Tim Kelly, Bridget Kingham, Ian MacKenzie and Dr Paul Rasmussen
Sydney Water	Heri Bustamante, Steven Lin, Mark Ognibene, Dammika Vitanage, Wanxin Wang and Wasantha Wicks
Toowoomba Regional Council	Alan Kleinschmidt and John Paulger
Western Australian Water Corporation	Claire Camplin, Lyndon Clark, Margaret Domurad, Kay Hyde, Pardeep Kumar, Gabrielle O'Dwyer and Leah Rheinberger

8.3 UNITED STATES OF AMERICA NITROUS OXIDE RESEARCH

This work was funded by the Water Environment Research Foundation under Project U4R07 and the Climate Change program. The members of the project team for this study were:

Principal authors:	Kartik Chandran, Ph.D. (Columbia University)
Field researchers:	Joon Ho Ahn, Ph.D. (Columbia University) Sungpyo Kim, Ph.D. (Columbia University) Hongkeun Park, Ph.D. (Columbia University) Brian Rahm, Ph.D (Columbia University)
Laboratorium researchers	Ran Yu, Ph.D. (Columbia University) Huijie Lu, Ph.D. (Columbia University)
Technical Review and Direction:	Greg Adams, P.E. (Los Angeles County Sanitary District) Eugenio Geraldo, Ph.D. (American Water) William Hiatt, Ph.D., P.E. Sudhir Murthy, Ph.D., P.E.(DC Water) Denny Parker, Ph.D. P.E.(Brown and Caldwell) Peter Strom, Ph. D. (Rutgers University) Jeff Weiss, Ph.D. (Los Angeles County Sanitary District)

8.4 UNITED STATES OF AMERICA METHANE RESEARCH

This work was funded by the Water Environment Research Foundation under Project U2R08 and the Climate Change program. The members of the project team for this study were:

Principal authors:	John Willis, P.E. (Brown and Caldwell)
Field assistants:	Anup Shah (Brown and Caldwell)
Technical Review and Direction:	Bob Forbes, PE (CH2M-Hill) Eugenio Geraldo, Ph.D., (American Water) Catherine O'Connor, (Metropolitan Water Resources District of Greater Chicago) Eliza Jane Whitman, PE (Parsons) Patrick Wootton, (GE)

8.5 RESEARCH PERFORMED IN THE NETHERLANDS

The authors acknowledge the contribution of Kyra Schipper, Pieter Vijfhuizen in the collection of field data. The Steering Committee of the project, Alex Sengers, Klaas Appeldoorn, Frank Brandse and Hardy Temmink are thanked for their constructive input during the project. The plant operators at Kralingseveer, Kortenoord and Papendrecht WWTP are also acknowledged for their hospitality and co-operation.

9

REFERENCES

- Ahn, J.-H., Kim, S., Pagilla, K., Katehis, D., Chandran, K., 2009, Spatial and temporal variability in N₂O generation and emission from wastewater treatment plants. Nutrient Removal Conference. Washington D.C., Water Environment Federation
- Andrews, J. Chambers, B., Davey, A., Galletti, S., Hobson, J., Hunt, D., Thorman, R., Walker, I., 2009, Carbon Accounting in the Water Industry; non-CO₂ Emissions, UKWIR, London
- Burgess, J.E., Colliver, B.B., Stuetz, R.M., Stephenson, T., 2002, Dinitrogen oxide production by a mixed culture of nitrifying bacteria during ammonia shock loading and aeration failure, *Journal of Industrial Microbiology & Biotechnology* 29, p 309 – 313.
- Casey, T. G., Wentzel, M. C., and Ekama, G. A., 1999a, Filamentous organism bulking in nutrient removal activated sludge systems - Paper 10: Metabolic behaviour of heterotrophic facultative aerobic organisms under aerated/unaerated conditions. *Water Sanitation* 25 (4), 425-442.
- Casey, T. G., Wentzel, M. C., and Ekama, G. A., 1999b, Filamentous organism bulking in nutrient removal activated sludge systems Paper 9: Review of biochemistry of heterotrophic respiratory metabolism. *Water Sanitation* 25 (4), 409-424.
- Chandran, K., 2010, Greenhouse nitrogen emission from wastewater treatment operations, WERF report U4R07a.
- Czepiel, P.M., Crill, P.M., Harriss, R.C., 1993, Methane emissions from municipal wastewater treatment processes, *Environmental Science Technology*, 27 p.2472 – 2477.
- Foley, J., and Lant, P., 2008. Fugitive Greenhouse Gas Emissions from Wastewater Systems: WSAA Literature Review No.01. Water Services Association of Australia, Melbourne.
- Foley, J., Lant, P., 2009, Direct Methane and Nitrous oxide emissions from full-scale wastewater treatment systems, Occasional paper No.24, Water Service Association of Australia.
- Gray, N.D., Miskin, I.P., Kornilova, O., Curtis, T.P., Head, I.M., 2002, Occurrence and activity of Archaea in aerated activated sludge wastewater treatment plants, *Environmental Microbiology* 4 (3), p.158 – 168.
- Guisasola, A., Haas, de D., Keller, J., Yuan, Z., 2008, Methane formation in sewer systems, *Water Research* (42) p 1421 – 1430.
- Gutierrez, O., Park, D., Sharma, K. R. and Yuan, Z., 2009, Effects of long-term pH elevation on the sulphate-reducing and methanogenic activities of anaerobic sewer biofilms. *Water Research* 43(9): 2549-2557
- GWRC, 2011, N₂O and CH₄ Emission from Wastewater Collection and Treatment Systems, Technical report, London, United Kingdom, ISBN 978 – 90 – 77622 – 24 – 7.
- Hvitved-Jacobsen, T., 2002, Sewer processes: microbial and chemical process engineering of sewer networks. CRC Press, USA.

- IPCC, 2006a. Ch.6 - Wastewater Treatment and Discharge. in H. S. Eggleston, L. Buendia, K. Miwa, T. Ngara, and K. Tanabe, editors. 2006, IPCC Guidelines for National Greenhouse Gas Inventories, Prepared by the National Greenhouse Gas Inventories Programme, vol.5 - Waste. IGES, Japan.
- IPCC, 2006b. Vol.1 - General Guidance and Reporting. in H. S. Eggleston, L. Buendia, K. Miwa, T. Ngara, and K. Tanabe, editors. 2006, IPCC Guidelines for National Greenhouse Gas Inventories, Prepared by the National Greenhouse Gas Inventories Programme, IGES, Japan.
- IPCC (2007), Fourth Assessment Report (AR4), Climate Change 2007: Synthesis report.
- Jiang, G., Gutierrez, O., Sharma, K. R. and Yuan, Z., 2010, Effects of nitrite concentration and exposure time on sulfide and methane production in sewer systems. *Water Research*, 44 (14): 4241-4251.
- Kampschreur, M.J., Temmink, H., Kleerebezem, R., Jetten, M.S., van Loosdrecht, M.C., 2009, Nitrous oxide emission during wastewater treatment, *Water Research* 43 (17), p. 4093 – 4103.
- Kampschreur, M.J., 2010, Dynamics of nitric oxide and nitrous oxide emission during nitrogen conversion processes, PhD thesis Delft University of Technology.
- Lens, P.N., De Poorter, M.-P., Cronenberg, C.C., Verstraete, W.H., 1995, Sulfate reducing and methane producing bacteria in aerobic wastewater treatment systems, *Water research* (29-3) p. 871 – 880.
- Tata, P., Witherspoon, J., Lue-Hing, C. (Eds.), 2003, VOC Emissions from Wastewater Treatment Plants, Boca Raton, FL, Lewis Publishers.
- Tallec, G., Garnier, J., Billen, G., and Gossais, M., 2006. Nitrous oxide emissions from secondary activated sludge in nitrifying conditions of urban wastewater treatment plants: Effect of oxygenation level. *Water Research* 40 (15), 2972-2980.
- Tchobanoglous G & F L Burton, 2003, Wastewater engineering – Treatment and reuse Metcalf & Eddy, Inc. 4th edition 2003. MacGraw-Hill, New York 2003
- Voorhuizen van, E.M., van Leusden, M., Visser, A., Kruit, J., Kampschreur, M., Dongen van, U., Loosdrecht van, M., 2010, Emissies van broeikasgassen van rwzi (in Dutch, summary in English), STOWA report 2010-08.
- VROM, 2008, Protocol 8136 Afvalwater, t.b.v. NIR 2008, uitgave maart 2008; 6B CH₄ en N₂O uit afvalwater (in Dutch).
- UNFCCC, 2007, Uniting on climate. United Nations Framework Convention on Climate Change, Bonn.
- Yu, R., Kampschreur, M.J., Loosdrecht, M.C.M.V., Chandran, K., 2010, Mechanisms and Specific Directionality of Autotrophic Nitrous Oxide and Nitric Oxide Generation during Transient Anoxia. *Environmental Science Technology*, 44, 1313-1319.
- Zhang L., Keller, J. and Yuan, Z., 2009, Inhibition of sulphate-reducing and methanogenic activities of anaerobic sewer biofilms by ferric iron dosing. *Water Research* 43(17): 4123-4132.

ANNEX 1

SAMPLE COLLECTION WITH GAS HOODS

SAMPLE COLLECTION FRANCE

The way the samples were taken for N_2O analysis depended on whether the surface was aerated or non-aerated. Both protocols are described below.

Sample collection from aerated surfaces

The square wooden *sampling box* (1m * 1m) is used in aerated conditions (see Figure 19). A pipe connected to a gas mass counter allows the flow of air supplied by the aeration system - "real" Q - to be collected and quantified (in m^3/h). A spur from this pipe allows the sample of air to be directed to the gas analyzer.

FIGURE 19

SAMPLING BOX FOR AERATED SURFACES



Sample collection from non-aerated surfaces

In case of non-aerated surfaces the sampling system used was the Odoflux dynamic flow chamber (see Figure 20).

FIGURE 20

SAMPLING BOX FOR NON-AERATED SURFACES



The flow chambers covered an area to be studied as hermetically as possible in order to isolate the surface from external conditions. The gases emitted by the isolated surface are collected by a vector gas which is injected into the chamber (Q1). The mixture of vector gas and gaseous effluent is then collected for analysis. The flow chamber used consists of an acrylic resin cylinder capped by a hemisphere, also of acrylic resin. The air-tightness of these two parts is ensured by polypropylene screws. The sweep air supply is fed by a pipe coiled against the wall and pierced with holes (flow Q1). The air sample is taken at the top of the hemisphere by means of a probe which has several holes along its length in order to ensure homogeneous sampling. The air is sucked in at flow Q2, of which 1l/min is directed to the analyser; the other part (Q2 - 1l/min) is released into the atmosphere.

To respect “pseudo-isokinetic” conditions, the applied flow Q1 must be equal to the flow sucked in Q2. The protocol developed in the framework of this project for measuring GHG recommends a relatively weak flow (Q1 = Q2) of the order of 3 to 10l/min; this flow thus ensures “static chamber” conditions in which the surface of the liquid is not disturbed and the surface emissions are very slightly diluted.

ANALYSIS N₂O IN LIQUID PHASE

The protocol for the analysis of dissolved N₂O presented here was drawn up by the Rennes CEMAGREF. The water samples are taken and conditioned in 330ml flasks, sealed hermetically with a septum. The sample conditioning stages are detailed below

- Weigh 100g of water sample in a 330ml glass flask.
- Add 1 drop of sulphuric acid and close the flasks hermetically (stopper + septum).
- Place the samples in a container with warm water at 80°C for 1hr, the dissolved N₂O is then released into the head space.
- The gaseous fraction in the head space is then sampled using a gas syringe and injected into three 3ml pill-boxes which have been previously conditioned in a vacuum;
- The analysis of the dissolved N₂O is done by gas chromatography - electron capture detector (GC/ECD) by the Rennes CEMAGREF, in France.

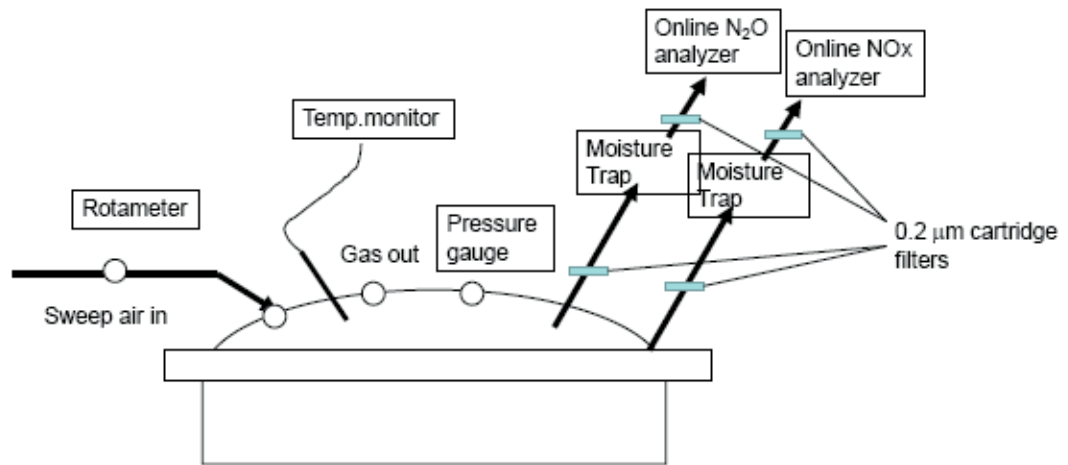
SAMPLE COLLECTION UNITED STATES OF AMERICA

Sampling procedures-headspace gas measurement

The overall procedure for measuring N₂O, NO and NO₂ fluxes from the head-space of activated sludge tanks involves a variant of the EPA/600/8-86/008 and the South Coast Air Quality Management District (SCAQMD) tracer methods. This variant was developed to measure those sources that have a relatively high surface flux rate when compared to diffusion (for instance, spilled oil containment).

Commercially available replicas of the US EPA surface emission isolation flux chamber (SEIFC, Figure 21) were used to measure gaseous N fluxes from activated sludge reactors.

FIGURE 21

SCHEMATIC OF FLUX-CHAMBER EMPLOYED FOR N₂O MEASUREMENT


The SEIFC consists of a floating enclosed space from which exhaust gas is collected in a real-time or discrete fashion. Since the surface area under the SEIFC can be measured, the specific flux of the gaseous compound of interest can be indirectly determined. The SEIFC ‘floats’ on the activated sludge tank surface and several replicate measurements can be taken at different locations in a single tank as well as from different tanks (nitrification, denitrification) along a treatment train.

The SEIFC is also equipped with mixing (physical mixer or via sweep gas circulation) to ensure adequate gas mixing and in some cases, an online temperature probe. The SEIFC is currently one of the few devices accepted by the USEPA for measuring gaseous fluxes (Tata et al., 2003) and as such it was employed for this study.

ANNEX 2

ABBREVIATIONS AND GLOSSARY

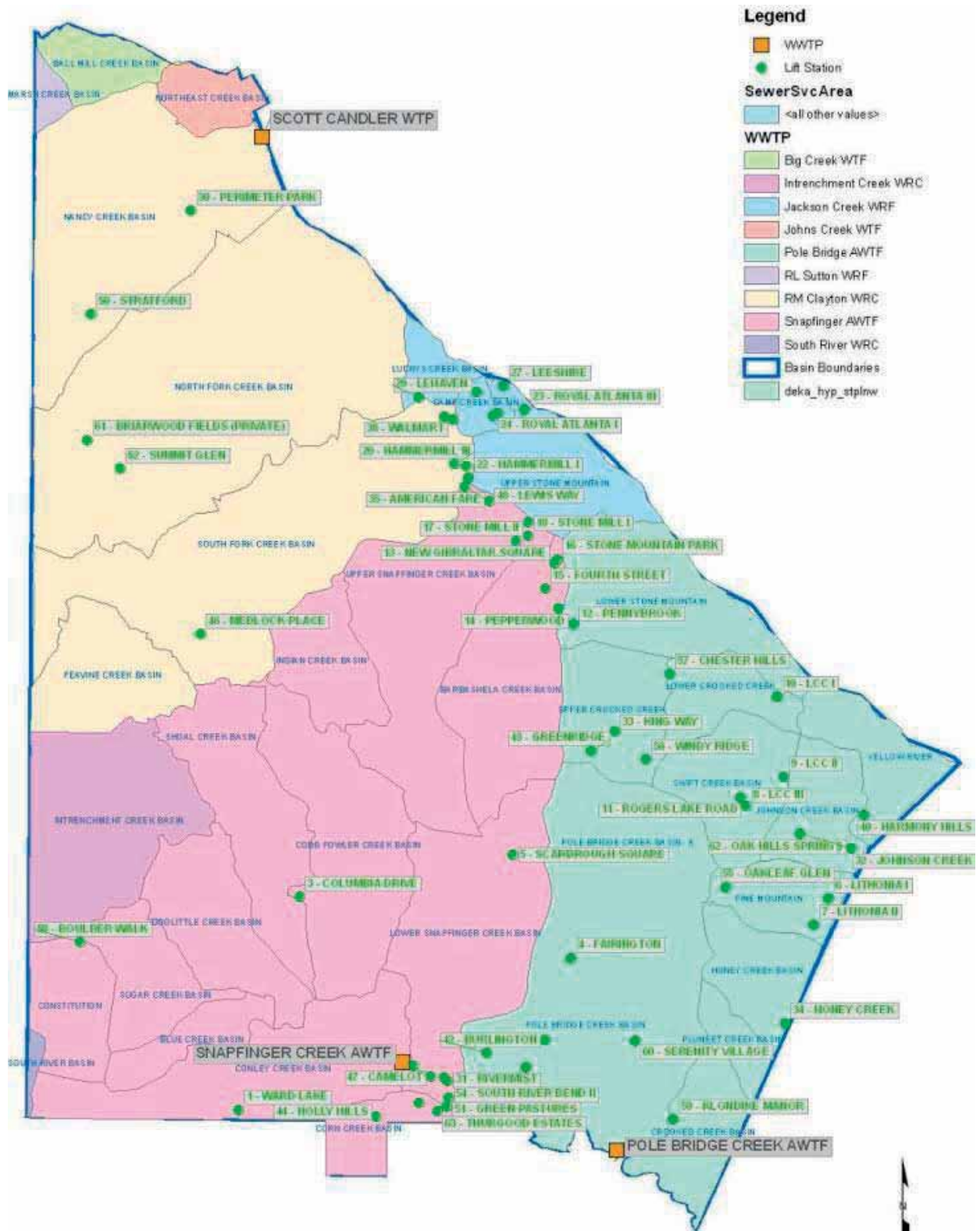
Abbreviation / term	
A/O and A ² /O	Type of WWTP configuration for the biological removal of phosphate ¹⁾
ADEME	French Environment and Energy Management Agency
Bardenpho	Type of WWTP configuration for the biological removal of phosphate ¹⁾ . Can be designed with different amount of stages.
BNR	Biological Nitrogen Removal
CH ₄	Methane
CO ₂	Carbon Dioxide
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
EPA	Environmental Protection Agency
FB	Fermentative Bacteria
Fe ^{2/3+}	Iron
FID	Flame Ionization Detector
GC	Gas Chromatograph
GF _{WWTP}	Generation factor (N ₂ O) for whole WWTP
GHG	Greenhouse Gas
H ₂ S	Hydrogen Sulphide
HRT	Hydraulic Retention Time
IPCC	Intergovernmental Panel on Climate Change
Johannesburg	Type of WWTP configuration ¹⁾
K _L a	Mass transfer coefficient (liquid → gas)
LCC - PS	Lower Crooked Creek Pump Station
MBR	Membrane Bioreactor
MLE	Modified Ludzack-Ettinger (i.e. a configuration type) ¹⁾
NH ₄ (-N)	Ammonium
NKj	Nitrogen Kjeldal
NGERS	National Greenhouse and Energy Reporting System
NO ₂ (-N)	Nitrite
NO ₃ (-N)	Nitrate
N ₂ O	Nitrous Oxide
SBR	Sequenced Batch Reactor
SEIFC	Surface emission isolation flux chamber
SRB	Sulphate Reducing Bacteria
SRT	Sludge retention time
TKN	Total Kjeldahl Nitrogen
VFA	Volatile Fatty Acids
USEPA	United States Environmental Protection Agency
WWTP	Wastewater Treatment Plant

1) For more information see: Tchobanoglous, G., 2003

ANNEX 3

DEKALB COUNTY'S COLLECTION SYSTEM

FIGURE 22 MAP OF DEKALB COUNTY'S COLLECTION SYSTEM.



ANNEX 4

CHARACTERISTICS WWTPS INVESTIGATED IN N₂O RESEARCH

Country	Type of process	Sludge load ¹⁾ (kg TKN _{in} · kg d.w. ⁻¹ · d ⁻¹)	Temperature SRT (appr.) (°C)	Effluent TN ¹⁾ (mg/l)	Process description
Australia	1. Ox.Ditch (4 rounds) ²⁾	0.043 0.042 0.03 0.042	23	3	Inlet works, anaerobic contact tank, 2 x extended aeration oxidation ditches (in parallel) with diffused aeration, secondary sedimentation; mechanical sludge thickening and dewatering.
	2. Johannesburg (3 rounds)	0.012 0.01 0.013	21	5	Inlet works, 2 x extended aeration Johannesburg bioreactors (in parallel) with submerged aspirating OKI [®] aerators, secondary sedimentation, sludge thickening, aerobic digestion, mechanical and solar dewatering.
	3. SBR (3 rounds)	0.021 0.017 0.021	20	15	Inlet works, primary sedimentation, sequencing batch reactor (4 compartments) with diffused aeration and bio-selector zone, sludge thickening, anaerobic digestion and mechanical dewatering.
	4. MLE-1 (1 round)	0.031	21	12	Inlet works, primary sedimentation, 11 x covered Modified Ludzack Ettinger (MLE) bioreactors (in parallel) with diffused aeration, secondary sedimentation, sludge thickening, mechanical dewatering and lime stabilisation.
	5. MLE-2 (4 rounds)	0.06 0.065 0.072 0.07	20	11	Inlet works, primary sedimentation, 2 x Integrated Fixed Film Activated Sludge bioreactors + 1 □ MLE bioreactor (in parallel) with diffused aeration, secondary sedimentation, sludge thickening and anaerobic digestion.
	6. MLE-3 (3 rounds)	0.01 0.01 0.012	18	13	Anaerobic lagoon, 1 x MLE bioreactor with diffused aeration, secondary sedimentation, maturation lagoons, and sludge wasting to an aerated facultative lagoon.
	7. A ² /O (2 rounds)	0.009 0.01	21	3	Inlet works, 2 x parallel trains: 1) Primary sedimentation, 4-stage Bardenpho bioreactor with diffused aeration, secondary sedimentation; 2) Pre-fementer, four-stage bioreactor (similar to A ² /O configuration) with diffused aeration and supplemental COD dosing by primary sludge from Train 1, secondary sedimentation, tertiary filtration, sludge thickening, aerobic digestion, sludge lagoon and mechanical dewatering.
	1. A ² /O	n.a.	n.a.	n.a.	Three-zones completely Stirred Tank Reactor. (anaerobic- anoxic- aerobic with sequenced aeration)
	2. A/O	n.a.	n.a.	n.a.	Plug flow process (anoxic –aerobic)
	3. A ² /O	n.a.	n.a.	n.a.	Three-zone completely Stirred Tank Reactor (anaerobic- anoxic- aerobic with sequenced aeration)
USA	4. ?? / MBR				Activated sludge with sequenced aeration followed by MBR
	1. Separate stage BNR (2 rounds) ²⁾	n.a.	15 23		The low-rate separate-stage nitrification denitrification process at this WWTP was sampled. The process was configured as a sequence of five reactors in series. The influent to this process consisted of the clarified effluent from an upstream high-rate process, mainly engaged organic carbon removal. The influent was fed in a step-feed fashion to the first two aerobic zones. The last three zones of this process were non-aerated and the second non-aerated zone received methanol to promote denitrification. The effluent channel of this process was aerated prior to secondary clarification.

Country	Type of process	Sludge load ¹⁾ (kg TKN _{in} · kg d.w. ⁻¹ · d ⁻¹)	Temperature (°C)	SRT (appr.) (d)	Effluent TN ¹⁾ (mg/l)	Process description
	2. Four-stage Bardenpho (2 rounds)	n.a.	14 23			The four-stage Bardenpho process consisted of pre-denitrification (without external carbon addition) followed by a primary aerated zone. The effluent of the primary aerated zone was internally recycled to the anoxic zone. Following the primary aerated zone was a de-oxygenation zone to scavenge dissolved oxygen, prior to methanol addition for enhanced denitrification. The final zone in this process was aerated primarily for stripping off the dinitrogen gas produced during denitrification, prior to secondary clarification
	3. Step-feed BNR 1 (2 rounds)	n.a.	19 25			The four-pass step-feed BNR process sampled consisted of pre-anoxic zones comprising about 1/3 of the pass volume followed by aerated zones. The transition zone between each pass was non-aerated to facilitate deoxygenation. The approximate influent flow split was 10%-40%-30%-20% to passes A, B, C and D, respectively. Pass A also received pre-settled anaerobic digestion centrate, which constituted approximately 30% of the influent TKN load to the process. Return activated sludge was also fed to Pass A.
	4. Step-feed non BNR (2 rounds)	n.a.	17 26			The step-feed non-BNR process sampled was configured and operated in four-pass step-aeration mode. The process was completely covered primarily for odor control. The headspace off-gases were consolidated and fed to a biofilter. The approximate influent flow split was 10%-40%-30%-20% to passes A, B, C and D, respectively. Return activated sludge was fed to Pass A.
	5. Separate centrate (2 rounds)	n.a.	30 34			The separate centrate treatment process was operated to process pre-settled anaerobic digestion centrate and partially convert the influent NH ₄ ⁺ -N to NO ₂ ⁻ -N. The separate centrate treatment process was operated in plug flow mode. Effluent from the separate centrate tank was fed to the overall plant return activated sludge line for possible bioaugmentation with primarily ammonia oxidizing bacteria (AOB) and for nitrogen removal via the short-cut nitrite pathway.
	6. Plug flow 1 (2 rounds)	n.a.	11 23			The first plug-flow process sampled was designed and operated primarily for organic carbon removal and nitrification and did not have dedicated anoxic zones or external organic carbon addition. The process was configured in four-pass mode.
	7. Plug flow 2 (2 rounds)	n.a.	11 22			The second plug-flow process sampled was also designed and operated for organic carbon removal and nitrification and did not have dedicated anoxic zones or external organic carbon addition. The process was configured in two-pass mode.
	8. MLE-1 (1 round)	n.a.	26			The first modified Lutzack Ettinger (MLE) process sampled was originally designed for operation in enhanced biological phosphorous removal mode, but subsequently operated in MLE mode. The process consisted of pre-denitrification without external organic carbon addition. Biomass from zone 6, which was aerated, was internally recycled to anoxic zone 2. Return activated sludge was fed to anoxic zone 1.
	9. MLE-2 (1 round)	n.a.	26			The second modified Lutzack Ettinger (MLE) process sampled was also originally designed for operation in enhanced biological phosphorous removal mode, but subsequently operated in MLE mode. The process consisted of pre-denitrification without external organic carbon addition. Biomass from zone 6, which was aerated, was internally recycled to anoxic zone 2. Return activated sludge was fed to anoxic zone 1.

Country	Type of process	Sludge load ¹⁾ (kg TKN _{in} ·kg d.w. ⁻¹ ·d ⁻¹)	Temperature SRT (appr.) (°C)	Effluent TN ¹⁾ (d)	Process description	
Netherlands	10. Step-feed BNR 2 (1 round)	n.a.	29	(mg/l)	The second step-feed process sampled was configured in four-pass mode. Each pass consisted of pre-anoxic zones comprising 1/3 of the pass volume followed by aerobic zones. The approximate influent flow split was50%-30%-20%-0% to passes A, B, C and D, respectively. The anoxic zones were mixed via low intensity pulse aeration. The return activated sludge was fed to Pass A.	
	11. Oxidation ditch (1 round)	n.a.	19		The oxidation ditch process was operated to achieve simultaneous nitrification and denitrification by operation are uniformly low aeration intensities and dissolved oxygen concentrations. The influent flow to the process was fed to the inner loop and was mixed and circulated using surface mixers. No external organic carbon was added to enhance denitrification. Return activated sludge was fed to the inner loop of the process.	
	12. Step-feed BNR 3 (1 round)	n.a.	24		The third four-pass step-feed BNR process sampled consisted of pre-anoxic zones comprising about 1/3 of the pass volume followed by aerated zones. The approximate influent flow split was 33.3%-33.3%-33.3%-0% to passes A, B, C and D, respectively. Pass A also received pre-settled anaerobic digestion centrate, which constituted approximately 40% of the influent TKN load to the process. Return activated sludge was also fed to Pass A. The reactors of this process were also covered and thus only composite measurements of the overall headspace could be performed.	
	1. Carrousel N&P removal; Papendrecht	0.009	20	23	4	Upfront the carrousel with simultaneously nitrification/denitrification a selector and anaerobic reactor was situated.
	2. Carrousel N&P removal; Kortenoord	0.012	19	n.a.	2.2	Upfront the carrousel with simultaneously nitrification/denitrification a selector and anaerobic reactor was situated.
	3. BNR; Kralingseveer (2 rounds) ³⁾	0.024 (fall) 0.036 (winter)	18 9	20	8.3 (fall) 10.4 (winter)	In this BNR the following reactor sequence was present: selector, plug flow denitrification zone, plug flow nitrification with recycle to denitrification zone, two parallel carousels with simultaneous nitrification/denitrification.
1) Based on actual data during measurement campaigns. 2) Explanation rounds see table 2. 3) Measured once in fall and once in winter.						

1) Based on actual data during measurement campaigns. 2) Explanation rounds see table 2. 3) Measured once in fall and once in winter.

ANNEX 5

RESEARCH AREA METHANE RESEARCH AUSTRALIA

FIGURE 23 AERIAL PHOTOGRAPH OF THE C016 RISING MAIN. SAMPLES WERE COLLECTED FROM THE C016 PUMP STATION WET WELL (0 M), SAMPLE POINT 1 (AT 500M), SAMPLE POINT 2 (AT 1100M) AND SAMPLE POINT 3 (AT 1900 M)

